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Screening Study on Feasibility of Standards of Performance for Hydrofluoric Acid Manufacture

Research Corp of New England, Wethersfield, CT

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16. ABSTRACT

This report contains background information on the hydrofluoric acid manufacturing industry such as the number of plants, their size, and location. This information was obtained in the open technical literature and through visits to several typical plants.

The economic profile of the industry indicates there will be no growth in the next five years.

General description of the manufacturing process, emission sources, emission rates, and controls are the main part of the report. Detailed descriptions of processes, production, emissions, and control at eleven plants are compiled in EPA's confidential files. State and local emission regulations and emission source sampling and analysis methods are also discussed.

The background information has been used in a simple emission projection model (Model IV) to determine the emission reductions that could be achieved by the application of New Source Performance Standards.

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Screening Study on Feasibility of Standards of Performance for Hydrofluoric Acid Manufacture

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DISCLAIMER

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1.0 ABSTRACT

This report contains background information on the hydrofluoric acid manufacturing industry. This information was obtained in the open technical literature and through visits to several typical plants.

The economic profile of the industry indicates there will be no growth in the next five years.

General description of manufacturing process emission sources, rates and controls are the main part of the report. State and local emission regulations and emission source sampling and analysis methods are also discussed.

The background information has been used in a simple emission projection model (Model IV) to determine the emission reductions that could be achieved by the application of New Source Performance Standards.

2.0 EXECUTIVE SUMMARY

Industry's Economic Profile

In the United States at the present time, there are 9 hydrofluoric acid (HF) plants in operation. Two are located in Louisiana, 2 in Texas and 1 each in California, Kentucky, New Jersey, Ohio, and West Virginia. According to 1977 figures, the industry produced 268,000 tons of hydrofluoric acid, while 1975 data showed the annual capacity to be 369,000 tons. In recent years almost all HF produced is in the anhydrous form. Major HF uses are fluorocarbon production (39%), aluminum industry production (27%), and with the remaining being used for uranium enrichment, petroleum alkylation, stainless steel pickling and miscellaneous.

The fluorocarbon aerosol ban resulted in a 20% reduction in HF production. The volume of HF manufacture will be the same for at least the next 5 years. While new plants are not planned two plants are expected to be closed by mid 1979. The rest of the industry will increase the utilization of their capacity to compensate for the difference.

HF Manufacturing Process

HF is manufactured from fluorspar and sulfuric acid in a rotary kiln according to the endothermic reaction:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\ HF$$

The product anhydrite is either slurried and transferred to a gypsum pond, or neutralized and recovered in the solid form. HF gases are first scrubbed and cooled, and almost all HF is recovered in a condenser. The remaining HF and impurities are scrubbed in an acid scrubber while fluosilicic acid can be recovered in a water scrubber. Almost all processes used a tail gas scrubber before venting the gas to the atmosphere. Crude HF is distilled to a high purity for a further use.

Four major variations of HF manufacture are:

1. Buss Process
2. Typical Process (described by EPA)
3. Aluminum Fluoride Manufacture Process
4. Patented Process

HF can be recovered from a phosphate rock using silicon tetrafluoride (a by product), but the process is in the early stages of development.

Emission Sources and Rates

There are few sources of air emissions in a HF manufacture plant. The major source of particulate emission is fluorspar drying and handling. The literature suggests that the spar emission rate is about 20 lb/ton and emission data from typical plants indicate that this emission factor is realistic. The only point source of gaseous emission is from the tail gas scrubber. The emissions consist of small amounts of HF, SiF_4 and SO_2. The HF manufacturing process model shows that uncontrolled soluble fluoride emission is 52 lb F/ton of HF. Controlled emissions using a gas scrubber with 90% efficiency amount to 4 lb F/ton HF. Total annual emission of soluble fluoride from HF manufacture after currently used control is 700 tons F/year. The projection for the year 2000 shows 5300 tons F/year based on 6% yearly growth. Since this growth is probably unrealistic, this emission projection appears to be high.

Fugitive fluoride emissions are expected from process upsets, HF handling and the gypsum pond (with pH of 1).

The emission inventory for HF manufacturing plants is too unreliable to develop actual emission factors.

Control of Emissions

Particulate emissions for spar drying and handling are controlled with fabric filters and wet scrubbers. The best control appears to be the use of a fabric filter with 99% efficiency. The gaseous emissions are controlled with wet scrubbers. The best control technique is the use of a packed tower with about 5 transfer units using alkaline scrubbing liquid which can achieve an efficiency of 99% for removal of HF, SiF_4 and SO_2. HF fugitive emissions from a kiln under upset conditions are best controlled with a stand-by caustic scrubber. Liming of the gypsum pond to obtain a pH of 6 would prevent any HF or SiF_4 emission.

State and Local Emission Regulations

Although hydrofluoric acid manufacturing is regulated under the permit and particulate regulations of the states where operations exist, no state has yet adopted regulations which specifically address HF production. Rather, states treat HF manufacturing as a process industry for purposes of air pollution control regulations. An analysis of state regulations indicates that process weight and/or fluoride emissions standards apply to virtually all HF plants.

Emission Source Sampling and Analysis

Sampling and analysis methods for criteria pollutants, particulate, SO_2, No_x are covered under EPA Methods 5, (17), 6 and 7. Total fluoride is covered under EPA Method 13. TRC experience indicates that a simplified sampling train can be used for gaseous fluoride emissions measurement. Remote Optical Sensing of Emissions (ROSE) has been developed by EPA's Environmental Sciences Research Laboratory/RTP. This technique is well suited for the measurement of ambient fluoride concentrations, and it distinguishes between HF and SiF_4.

Emission Reduction With NSPS

Results of the Model IV calculation indicate that there would be no reduction in 1987 emission if NSPS are implemented. This is due to the projected lack of increase in production volume. Review of emissions control on an industry-wide basis shows that most plants are using best control technology. Since some plants have better controls in one area and some in the other NSPS would bring the plants on an equal level. It appears that fluoride emission would be reduced by 20-30% if best control technology was applied to all plants.

3.0 CONCLUSIONS AND RECOMMENDATIONS

3.1 Conclusions

1. No growth is expected in the HF manufacturing industry in the next 5 years. The growth after that is unpredictable but will be probably below 6% annually (an average for last 3 decades).
2. There are 4 variations in HF manufacture that are described in this report.
3. HF manufacturing has 2 major sources of emission: Particulate emissions from spar drying and tail gas from the HF absorption train.
4. The best control for particulate emissions are fabric filters and wet scrubbers for tail gas containing HF, SiF_4 and SO_2.
5. The quantitative data on gaseous emissions containing fluorides are virtually non-existent due to the lack of regulations.
6. It is unclear whether the fluorspar should be included in the fluoride emissions and what is its effect on vegetation, animals and man.
7. The major problem in HF manufacturing is corrosion which can result in HF emissions. Good maintenance is essential for proper operation.
8. The major benefit of NSPS for this industry would be to equalize emissions controls throughout the industry resulting in overall 20-30% reduction in fluoride emission in the existing plants.

3.2 Recommendations

In order to obtain a better understanding of HF manufacture environmental problems the following are recommended:

1. Measure fluoride concentrations in tail gas from HF manufacture.
2. Quantify fugitive emissions in HF manufacture.
3. Determine fluorspar effects and whether they should be considered fluorides or particulates.

4.0 HYDROFLUORIC ACID MANUFACTURING INDUSTRY - ECONOMIC PROFILE AND STATISTICS

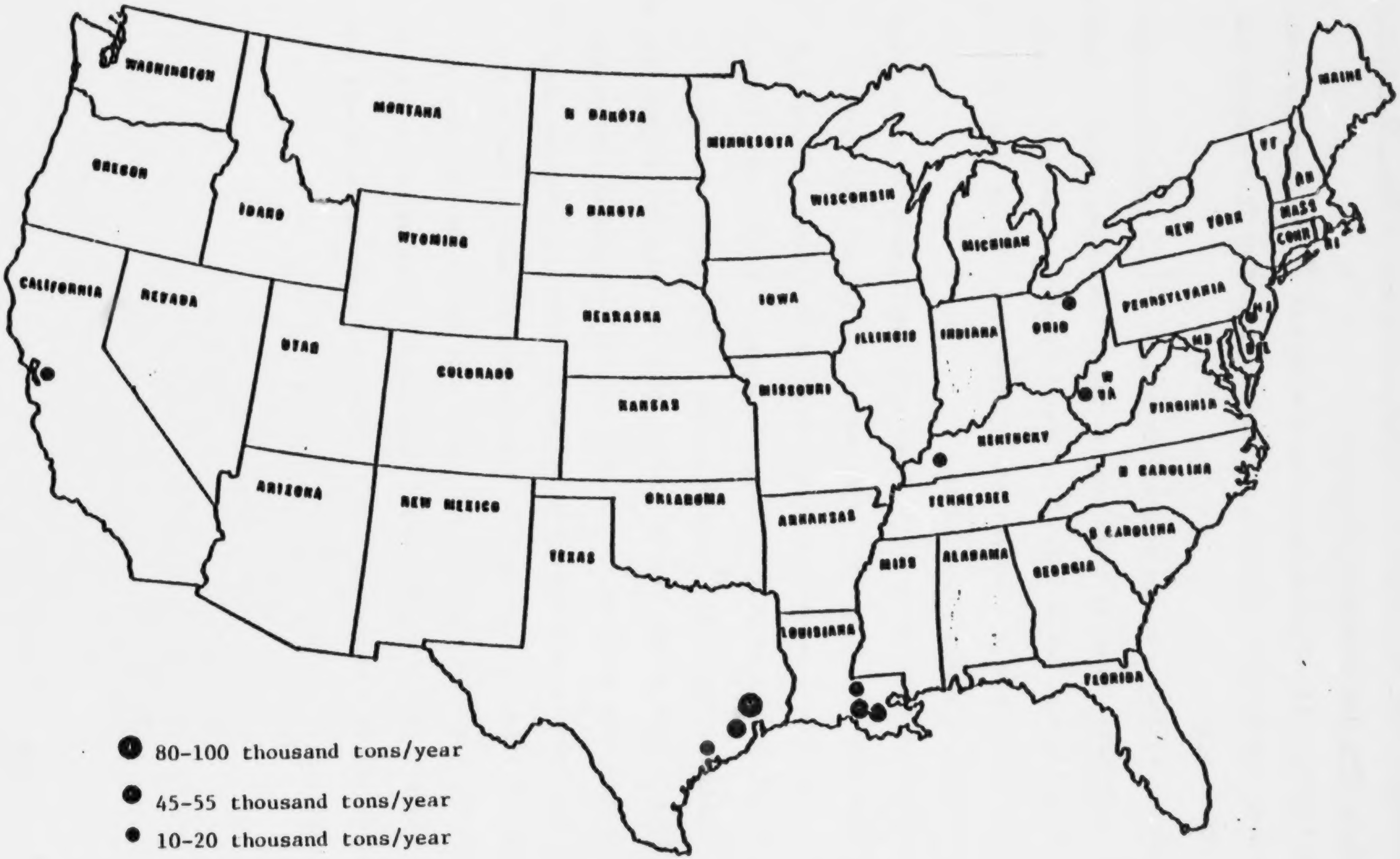
4.1 Industry Size and Geographic Location

Hydrofluoric acid (HF) manufacturing is a segment of the inorganic chemical industry under the Standard Industrial Classification (SIC) 2819 - Industrial Inorganic Chemicals.

In the United States at the present time, there are 11 hydrofluoric acid plants in operation. Three of these are located in Louisiana, three in Texas and one each in California, New Jersey, Ohio, West Virginia and Kentucky. Figure 4-1 illustrates the approximate locations and relative size of each plant as determined by 1975 annual capacity statistics.

The term "HF Manufacturing Plant" needs some clarification. All HF manufacturing facilities are a part of large chemical plants and only 20 to 90 employees out of several hundred are involved in HF production. In several plants HF is a link in a production chain consisting of H_2SO_4 - HF - fluorocarbons. In several plants all HF manufactured is used within the plant.

According to 1977 actual data determined from the industry 268,000 tons of hydrofluoric acid were produced for internal use and for outside consumption. In spite of the aerosol controversy, fluorocarbon production consumed about 39% of the total hydrofluoric acid supply. The aluminum industry accounted for about 272%. The remainder of the hydrofluoric acid supply was utilized for uranium enrichment (6%), stainless steel pickling (2%), alkylation of olefins (4%) and miscellaneous application (22%). [Table 4-1 presents the annual capacity for each plant.]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ARIZONA
NEW MEXICO
OKLAHOMA
ARKANSAS
S CAROLINA
TEXAS
MISS
ALABAMA
GEORGIA
LOUISIANA
FLORIDA
● 80-100 thousand tons/year
● 45-55 thousand tons/year
● 10-20 thousand tons/year

Figure 4-1 Location and Relative Capacity of Hydrofluoric Acid Manuafacturers[9]

TABLE 4-1

HYDROFLUORIC ACID MANUFACTURING PLANTS IN THE UNITED STATES

Source: 1977 Directory of Chemical Products, U.S.A. Chemical Information Services, Stanford Research Institute

PRODUCER	LOCATION	ANNUAL CAPACITY (THOUSANDS OF TONS)	IN OPERATION SINCE
1. Allied Chem. Corp. Indust. Chems. Div.	1. Baton Rouge La.	20	1946
	2. Claymont Del.	25	
	3. Geismar, La.	45	1967
	4. Nitro, W.Va.	15	1959
	5. Pittsburg, Calif.	12	1952
Specialty Chems. Div.	6. Marcus Hook, Pa.	n.a.	
2. Aluminum Co. of America	Point Comfort, Tex.	55	1961
3. Ashland Oil, Inc. Ashland Chem. Co., div. Lehigh Valley Chem. Co. div.	Glendon, Pa.	5	
4. E. I. du Pont de Nemours & Co., Inc. Biochems. Dept.	La Porte, Tex.	100	1964
5. Essex Chem. Corp. Chems. Div.	Paulsboro, N.J.	11	
6. Kaiser Aluminum & Chem. Corp. Kaiser Chems. Div.	Gramercy, La.	50	
7. Kewanee Indust., Inc. Harshaw Chemical Co., subsid. Indust. Chems. Dept.	Cleveland, Ohio	18	1972
8. Pennwalt Corp. Inorganic Chem. Div.	Calvert City, Ky.	25	1949
9. Stauffer Chem. Co. Indust. Chem. Div.	Greens Bayou, Tex.	18	
	TOTAL	399	

Sources: Chemical Marketing Reporter, November 17, 1975 and communication with industry.

Comments:

1. Contacts with the industry indicate that 3 of above plants (Allied Chemical's, Claymont, and the Ashland plant) no longer manufacture HF. Consequently, total annual capacity without these plants is 369 thousand tons per year.
2. Actual total 1977 production (obtained under confidentiality agreement) is 268 thousand tons. The discreplancy is the result of erroneous annual capacity listing and capacity's underutilization.

4.2 Capacity Utilization and Consumption

The existing hydrofluoric acid plants have been underutilizing their capacity for the past several years. In 1977 the annual capacity of the industry totaled 369,000 tons, while total production amounted to 268,000 tons, or 73% of total capacity.

The major users of all of the marketed hydrofluoric acid are the aluminum and fluorocarbon industries. In aluminum manufacturing, the hydrofluoric acid is not used directly in the smelting process, but goes into producing aluminum fluoride and synthetic cryolite from reaction with alumina and caustic soda, respectively. These products together with bauxite are then used in the molten bath which undergoes electrolysis to produce aluminum.[2] An estimated 56 pounds of hydrofluoric acid are required to produce 1 ton of aluminum. Table 4-5 in Section 4.3 shows the production/consumption figures for the aluminum industry.

Fluoride production accounted for 42% of the total hydrofluoric acid supply in 1976.[2] Inorganic fluorides are manufactured for utlization as preservatives, insecticides, catalysts, fluxes, for steel pickling and for use in fire extinguishers. Hydrofluoric acid is used in the manufacture of elemental fluorine gas which in turn is used to manufacture uranium hexafluoride sulfur hexafluoride, halogen fluorides and emulsified perfluorochemicals. The organic fluorides, which utilize the rest of the available hydrofluoric acid, are manufactured for production of various chlorofluorocarbons. These fluorocarbons are widely used as refrigerants, aerosol propellants, resins, solvents and elastomers.[3]

The geographic location of the hydrofluoric acid plants is significant in determining the potential effects of atmospheric fluorides on plants and animals. Table 4-2 gives population statistics for 1 and 5 mile circles around each plant. The farm statistics give an indication of the amount of agricultural activity in the vicinity of each plant which may be subject to fluoride emissions.

Based on the number of employees involved in HF manufacture and actual production data, one can calculate that about 1.5 employees are needed to produce one thousand tons/year of anhydrous HF. This adds up to a total of 402 employees (nationwide) in HF manufacture.

TABLE 4-2

POPULATION STATISTICS
(based on TELE/SITE and contacts with the industry)

PLANT	LOCATION	EMPLOYEES IN HF MANUF.	POPULATION		FARM POPULATION	
			0-1 MILES	1-5 MILES	0-1 MILES	1-5 MILES
	Texas					
Alcoa	Point Comfort	5-1	0	8,386	0	21
DuPont	La Porte	90	13	41,335	0	4
Stauffer	Greens Bayou	n.a.*	2,454	105,894	0	20
	Louisana					
Allied	Geismar	15	0	5,312	0	64
Allied	Baton Rouge	30	1,375	178,292	0	285
Kaiser	Gramercy	n.a.	0	11,851	0	87
	California					
Allied	Pittsburg	25	28	41,079	0	56
	Kentucky					
Pennwalt	Calvert City	41	0	4,145	0	32
	New Jersey					
Essex	Paulsboro	n.a.	8,084	158,884	5	169
	Ohio					
Harshaw	Cleveland	20	16,631	479,543	17	216
	W. Virginia					
Allied	Nitro	25	1,972	39,904	1	12

---

*n.a. = not available.

4.3 Industry Growth Trends

The production of industrial inorganic chemicals depends upon a wide range of economic activities and does not rely on one specific sector of the economy. Presently, the largest consumers of hydrofluoric acid are the fluorocarbon and aluminum industries, accounting for 42% and 32% of the total hydrofluoric acid usage in 1976.[2] A good indicator of the hydrofluoric acid production trend is the consumption of acid-grade fluorspar used in its manufacture. Table 4-3 illustrates the production trend from 1972 through 1977.

TABLE 4-3

HYDROFLUORIC ACID PRODUCTION

1972 - 1977(2,3,4,5,6,7,8)

		1972	1973	1974	1975	1976	1977
Acid-Grade Fluorspar Consumed (Short Tons)		752,728	803,999	838,211*	673,626	631,300	560,519
HF Produced (Short Tons)	Withdrawn From System	248 879	269,153	281,620	229,247	202,644	182,690
	Not Withdrawn From System	93,270	96,301	99,385	84,138	85,518	73,000

*Derived by assuming 2.2 lb acid-grade fluorspar - 1 lb hydrogen fluoride

Early in 1975 a controversy arose concerning the use of fluorocarbon aerosols and their possible effect on the ozone layer of the stratosphere. As a result of the controversy, fluorocarbon aerosol sales decreased as did the demand for the hydrofluoric acid used in their manufacture. In April of 1977, the Food Drug Administration (FDA) and Consumer Product Safety Commission (CPSC) stated the need for warning labels to be placed on all products containing fluorocarbon propellants. Following this action in May of 1977 the EPA along with the FDA and the CPSC issued a set of rules which would ban fluorocarbon aerosol propellants for nonessential uses by December 15, 1978 and would prohit their shipment between states by April 15, 1978.[4] This ruling has had a significant effect on hydrofluoric acid production since 1975. This controversy has reduced the demand for HF by approximately 20%. The statistics for production of the controversial fluorocarbon F11 and F12 for 1976 and 1977 are shown in Table 4-4. An illustration of the reduction in fluorocarbon production is the fact that three plants have been closed since 1975 and production at one has declined 50%.

TABLE 4-4

1976 - 1977 PRODUCTION OF FLUOROCARBONS F11 and F12[3,4,5,6,7] (MILLION POUNDS)

	1976	1st Qtr. 1977	2nd Qtr. 1977	3rd Qtr. 1977	4th Qtr. 1977	Total 1977
Hydrofluoric Acid Consumed*	624	140	158	144	104	546
F11 & F12 Produced	218	49	55	50	36	191

*Derived by assuming .35 lbs HF = 1 lb fluorocarbon

Table 4-5 presents the production statistics for the aluminum industry from 1975 through 1977 and estimated production through 1982.

TABLE 4-5

ALUMINUM INDUSTRY PRODUCTION
1975 - 1982 (2,3,4,5,6,7)
(THOUSAND TONS)

	1975	1976	1977	1980[†]	1982[†]
Hydrofluoric Acid Consumed*	109	119	127	164	195
Aluminum Produced	3,880	4,250	4,530	5,857	6,964

*Derived by assuming 56 lb HF = 1 ton aluminum
(via cryolite and aluminum fluoride)
[†] Assume 9% increase each year

The economic strength in HF manufacturing is that it will be indispensable to the aluminum industry for many decades despite the introduction of aluminum process techniques that avoid HF.[9]

The major weakness is the enormous aluminum inventory surplus and the depressed economy. These factors are expected to keep the aluminum supply loose and production low for several years.

In conclusion it appears that HF manufacture will not increase for at least 5 years. Contacts with the industry revealed that 1982 production will stay on the 1977 level with a total of 254,000 tons. Two plants are expected to be closed by mid-1979. The rest of the industry will operate at a higher capacity to compensate for the difference. Contacts with HF manufacturers also indicate that no new facilities or modifications are expected in the next 5 years. The importation of HF is likely to increase.

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5.0 HYDROFLUORIC ACID MANUFACTURING PROCESS

5.1 Hydrofluoric Acid Manufacturing Chemistry

HF Properties

In volume of production, HF is the most important manufactured compound of fluorine.[1] Both the anhydrous and aqueous acids are used directly or as intermediates but anhydrous acid is becoming a principal product.

Anhydrous HF is a colorless liquid or gas (bp 19.5°C), highly water soluble and fuming strongly in contact with the atmosphere. The formula weight is 20.006, but hydrogen bonding between molecules produces extensive polymerization, and the liquid and gas show large departure from ideal behavior. As a matter of fact HF is the most imperfect gas studied.[2] The physical properties of anhydrous HF are shown in Table 5-1.

Fluorspar Properties

The preferred raw materials for the manufacture of HF in the United States are acid grade fluorspar and sulfuric acid. The physical properties of fluorspar are shown on Table 5-2.[3] The fluorspar is treated with sulfuric acid according to the endothermic reaction:

$$\mathrm{Ca\ F_2 + H_2SO_4 \rightarrow Ca\ SO_4 + 2\ HF}$$

The reaction is believed to take place in a sequence of steps[3]

$$\mathrm{Ca\ F_2 + H_2\ SO_4 \rightarrow Ca\ (HSO_4.F.HF)}$$

$$\mathrm{Ca\ (HSO_4.F) + HF \rightarrow Ca\ SO_4 + 2\ HF}$$

The ability of the reaction to proceed to the maximum degree in commercial operation is influenced by the purity and fineness of the fluorspar, the temperature of the reaction, the time allowed for completion of the reaction, and the intimacy of mixing of the acid and spar.

TABLE 5-1

THE PHYSICAL PROPERTIES OF ANHYDROUS HYDROGEN FLUORIDE[1]

formula weight (calculated)	20.006
molecular weight	
saturated vapor, at boiling point	78.24
saturated vapor, at 100°C	49.08
boiling point, at 1 atm	19.51°C
melting point	−83.37°C
density	
liquid, at 25°C	0.9576 g/cm^3
vapor, saturated, at 25°C	3.553 g/liter
vapor pressure, at 25°C	17.8 psia
heat of vaporization	
boiling point, at 1 atm	1609 cal/20.01 g 1785
heat of fusion, melting point	46.93 cal/g
heat capacity, constant pressure	
liquid, boiling point	12.2 cal/(20.01 g) (°C)
vapor, at 25°C, 1 atm	143 cal/(20.01 g) (°C)
heat of formation	
ideal gas, at 25°C[c]	−64.9 kcal/20.01 g
free energy of formation	
ideal gas, at 25°C[c]	−65.0 kcal/20.01 g
entropy, ideal gas, at 25°C[c]	41.5 cal/(20.01 g)(°C)
critical temperature	188°C
critical pressure	941 psia
critical density	0.29 g/cm^3
viscosity, at 0°C	0.26 cP
surface tension, at boiling point	8.6 dyn/cm
refractive index, 5893 Å, at 25°C	1.1574
molar refractivity (5893 Å, formula wt)	2.13 cm^3
conductivity, at 0°C	$<1.6 \times 10^{-6}$ mho/cm
dielectric constant, at 0°C	83.6
dipole moment, HF molecule	1.83 D

[a] From vapor pressure vs temperature.

[b] From calorimetry.

[c] The enthalpy change for the reaction HF (ideal gas) → HF (real gas), at 25°C, 1 atm, is uncertain, and may exceed several kilocalories per mole (20).

TABLE 5-2

THE PHYSICAL PROPERTIES OF FLUORSPAR (CaF_2)

Molecular weight - 78.08

Melting point 1418°C

Boiling point 2513°C

Density - 3.18 g/cm^3

Solubility of CaF_2 in Water

t°C	Gms. CaF_2 per liter sat. sol.	
0	0.013	(flurospar)
15	0.015	(fluorspar)
18	0.016	
18	0.018	
18	0.015	(calcined)
25	0.018	
25	0.016	(fluorspar)
25	0.040	(ph = 6.4)
40	0.017	(fluorspar)

Solubility of CaF_2 in Acetic Acid

	Gms. CaF_2 dissolved per 100 cc. in aqucous		
t°C	0.5 Normal CH_3COOH.	1.0 Normal CH_3COOH.	2.0 Normal CH_3COOH.
40............	0.0153	0.0175	0.0192
60............	0.0178	0.0203	0.0229
80............	0.0206	0.0237	0.0267
100............	0.0229	0.0264	0.0300

Solubility of CaF_2 in Hydrochloric Acid at 25°C

Normality of aq. HCl	Gm. moles CaF_2 Dissolved per liter	pH of sat. sol.
0.01	0.00087	2.02
0.10	0.0053	1.05
1.00	0.0280	0.04

Heat of Formation (Solid at 298°K - 290.3 Kcal/g mole)

Heat of Fusion - 7.10 Kcal/g mole

Heat of Vaporization - 83.0 Kcal/g mole

Entropy at 298°K - 16.4 eu.

5.2 Typical Hydrofluoric Acid Manufacturing Process

In reviewing the HF manufacturing process, a typical process schematic will be discussed first, followed by four major variation of the process. The initial intention was to present a process schematic for each plant and describe its process. However, since some companies consider their process description and schematic confidential, this was not feasible.

The first step in HF manufacturing is spar drying. Most of the plants import acid grade spar from Mexico, North Africa or Italy. The spar is received in the particle size needed for reaction and can be wet (10% moisture) or dry. Almost all plants have spar drying facilities. Spar dryers are usually rotary kilns internally heated and some employ an independent cooling kiln with a heat recovery system.

Sulfuric acid, a second raw material for HF manufacturing, is frequently manufactured at the same facility.

The schematic of a typical HF manufacturing process is shown in Figure 5-1. This process schematic applies in general to most HF manufacturing facilities. In recent years almost all HF is manufactured in anhydrous form; 70% acid is manufactured by dilution of anhydrous HF with water. The process schematics 6.2 showing the manufacture of 80% acid in strong acid absorbers and 50% HF in weak acid absorbers are becoming obsolete.

The reaction between spar and sulfuric acid in the kiln is endothermic and in most cases heat is supplied to speed up the reaction. To effect a release of over 98% of fluorine in the spar the reaction time is normally 30-60 minutes at 200-250°C with HF leaving the reactor at 100-150°C.

Since fluorine values dominate raw material costs, these factors are optimized to give the maximum yield of hydrogen fluoride.

Acid-grade fluorspar is a finely ground flotation product having the following typical specifications:

Screen analysis: 325 mesh. 1% on 100 mesh, 12% on 200 mesh, 30% on 250 mesh, 45% through

CaF_2	minimum 97.5-98%
SiO_2	maximum 1.0%
S	maximum 0.05%
H_2O	maximum 0.1%
$CaCO_3$	principal remainder

Silica is a highly objectionable contaminant, since each pound consumes 2.6 lb. of fluorspar and 3.3 lb. of sulfuric acid by the reaction:

$$SiO_2 + 2\ CaF_2 + 2\ H_2SO_4 \rightarrow SiF_4 + 2\ CaSO_4 + 2\ H_2O$$

When hydrogen fluoride containing SiF_4 is absorbed in water, a further loss of fluorine values occurs by the reaction:

$$SiF_4 + 2\ HF\ (aq) \rightarrow H_2SiF_6(aq)$$

Carbonates are harmful in consuming sulfuric acid, in producing foaming in the generator, and in contributing carbon dioxide to the gas stream where it acts as a noncondensible dilutent to the hydrogen fluoride. Sulfur-bearing minerals in fluorspar (e.g., galena, pyrites) may generate hydrogen sulfide or sulfur dioxide, contaminating the hydrogen fluoride, and sometimes causing deposits of sulfur in the gas-handling equipment.

Table 5-3 gives an extensive list of fluoride reactions many of which can take place in HF manufacturing.

Reproduced from best available copy.

TABLE 5-3[6]

Reactions of Fluorides

	Formation of Silicon Tetrafluoride In An Acid Medium
1.	$CaF_2 + H_2SO_4 = CaSO_4 + 2\ HF$
2.	$4\ HF + SiO_2 = SiF_4 + 2\ H_2O$
3.	$6\ HF + SiO_2 = H_2SiF_6 + 2\ H_2O$
4.	$H_2SiF_6 = SiF_4 + 2\ HF$
	Formation of Silicon Tetrafluoride in Thermal Processes
5.	$Na_2SiF_6 = 2\ NaF + SiF_4$
6.	$CaF_2 + 1/2\ SiO_2 = CaO + 1/2\ SiF_4$
7.	$CaF_2 + 3/2\ SiO_2 = CaSiO_3 + 1/2\ SiF_4$
8.	$CaF_2 + 1/2\ CaSiO_3 = 3/2\ CaO + 1/2\ SiF_4$
	Reactions of Silicon Tetrafluoride With Water
9.	$3\ SiF_4 + 2\ H_2O = 2\ H_2SiF_6 + SiO_2$
10.	$SiF_4\ (g) + 2\ H_2O\ (g) = SiO_2\ (s) + 4\ HF\ (g)$
	Formation of Boron Trifluoride
11.	$6\ CaF_2 + 5\ B_2O_3 = 4\ BF_3 + 3\ Ca_2\ B_2\ O_3$
	Formation of Hydrogen Fluoride By Hydrolysis
12.	$CaF_2 + H_2O = CaO + 2\ HF$
13.	$2\ NaF + H_2O = Na_2O + 2\ HF$
14.	$2/3\ AlF_3 + H_2O = 1/3\ Al_2O_3 + 2\ HF$
15.	$CaF_2 + H_2O + SiO_2 = CaSiO_3 + 2\ HF$
16.	$CaF_2 + H_2O + Al_2O_3 = Ca\ (AlO_2)_2 + 2\ HF$
17.	$Na_3AlF_6 + 2\ H_2O = Na\ AlO_2 + 2\ NaF + 4\ HF$
	Formation of Volatile Metal Fluorides
18.	$CaF_2 + Na_2SiO_3 = CaSiO_3 + 2\ NaF$
19.	$CaF_2 + K_2SiO_3 = CaSiO_3 + 2\ KF$
20.	$CaF_2 + Na_2CO_3 + SiO_2 = CaSiO_3 + CO_2 + 2\ NaF$
21.	$CaF_2 + 4/3\ Al_2O_3 = Ca(AlO_2)_2 + 2/3\ AlF_3$

The ratio of H_2SO_4 to CaF_2 is seldom stoichiometric, since, depending upon the relative cost of the two, one is used in slight excess. Recent practice has been to use excess acid. Almost all plants use externally heated horizontal kilns with spar fed continuously at the forward end by a screw conveyor. Acid is also added at the forward end of the kiln, and anhydrite is removed through an air lock at the opposite end. The anhydrite is then either slurred and transferred to system pond or recovered in the solid form. The gases emanating from the kiln are removed at the front end of the kiln. The gases consisting of HF, H_2O, SO_2, SiF_4, SO_2, H_2SO_4 and particulate are first treated in a precondenser or scrubber. The purpose of the precondenser is to remove particulate, water and sulfuric acid and to cool down the gas stream. The HF vapors are subsequently condensed in two refrigerant-chilled shell and tube condensers. The crude condensed HF represents almost 98% of production. It flows to intermediate storage tanks and is later distilled. The uncondensed gases from condensers enter a fresh H_2SO_4 absorption tower. The gas stream leaving the acid absorber contains most of the SiF_4 and enters two water scrubbers where fluosilicic acid is recovered. The gases are then vented into the atmosphere or are introduced into a caustic scrubber. The driving force for gas movement through the absorption train is provided by an ejector.

The total pressure drop across the HF absorption train is 15-20 inches W.G. The kiln is kept under negative pressure of 1/2 in W. G.

The crude HF obtained from the two condensers is distilled in two distillation columns to a purity of 99.98% making it the purest chemical in regular commercial distribution.

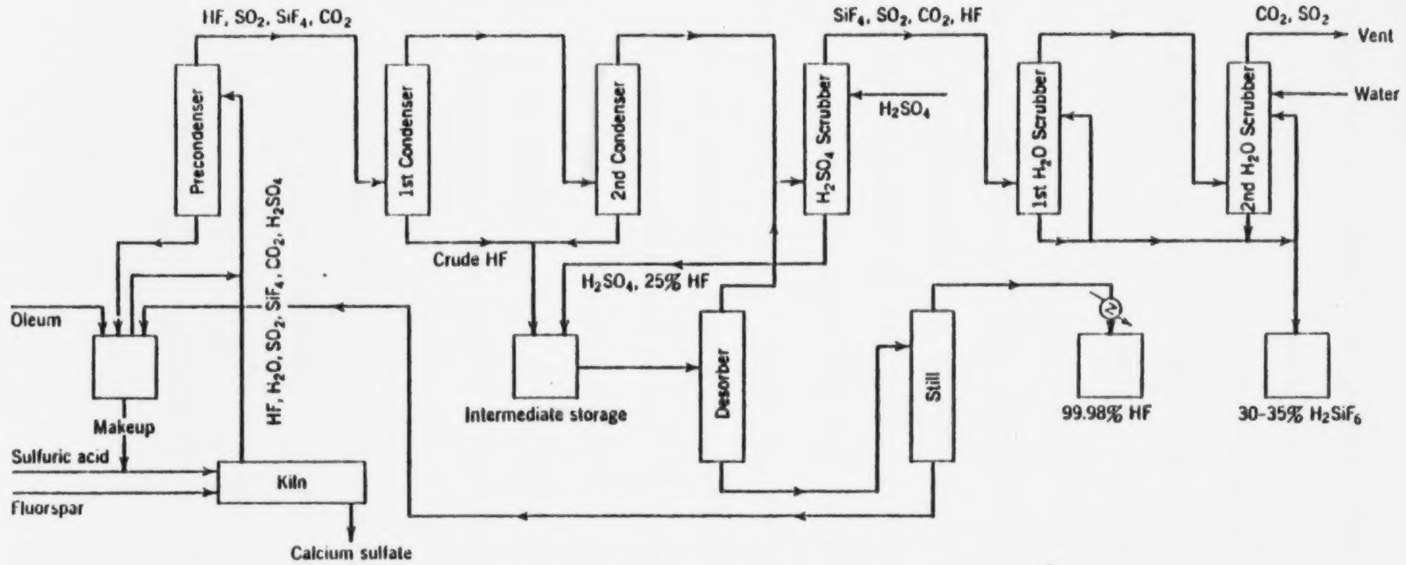

HF, SO_2, SiF_4, CO_2
Precondenser
1st Condenser
2nd Condenser
SiF_4, SO_2, CO_2, HF
H_2SO_4 Scrubber
H_2SO_4
1st H_2O Scrubber
2nd H_2O Scrubber
CO_2, SO_2
Vent
Water
Crude HF
H_2SO_4, 25% HF
Oleum
Makeup
Sulfuric acid
Fluorspar
Kiln
Calcium sulfate
HF, H_2O, SO_2, SiF_4, CO_2, H_2SO_4
Intermediate storage
Desorber
Still
99.98% HF
30-35% H_2SiF_6

Fig. 5-1 Schematic flow diagram for the manufacture of hydrogen fluoride.[1]

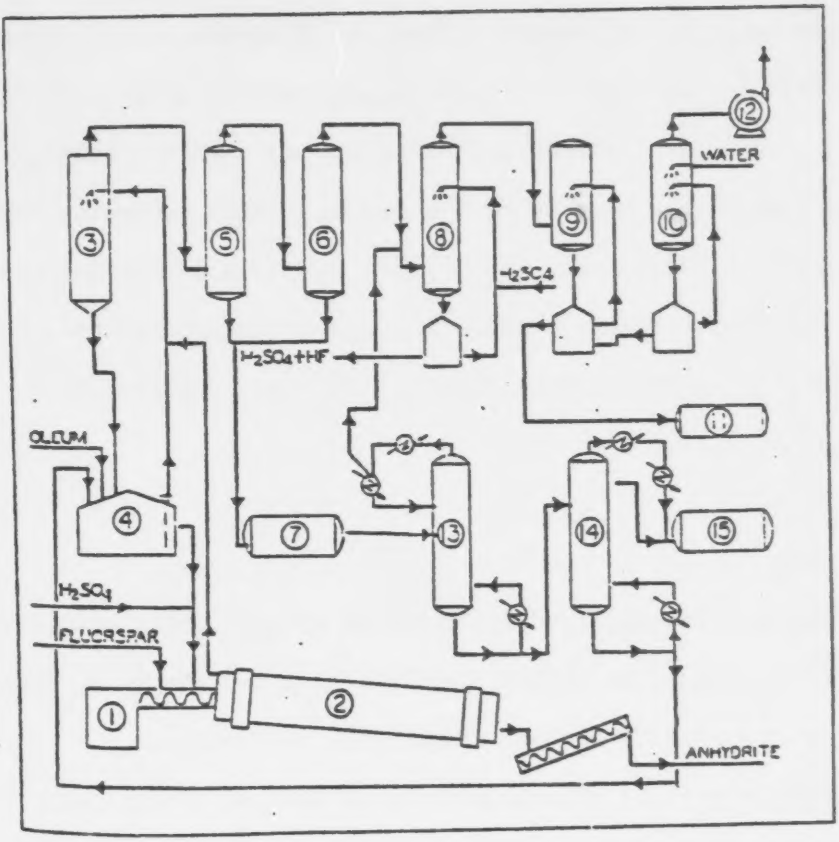
5.3 Major Variations of Hydrofluoric Acid Manufacturing Processes

Since it is not possible to present a specific HF manufacturing process schematic and description for each individual plant, four major process variations will be described. Only open literature information was used to describe these variations. Three plants were visited in the course of this screening study: Allied Chemical plants in Baton Rouge and Geismar, Lousiana and DuPont plant in La Porte, Texas. Reports of trips to these plants contain some confidential information and are not present in this report. The visit reports are a part of the EPA's confidential files.

a. Buss Process[3]

Figure 5-2 shows the process flow sheet for HF manufacturing using Buss technology. Since the process is almost identical to a typical HF process described in paragraph 5.2, only specifics of the process will be discussed.

One of the special features of this process is the use of a premixer called Ko-Kneader developed by the Buss Co. of Basle, Switzerland.


①
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⑩
⑪
⑫
⑬
⑭
⑮
WATER
H_2SO_4
H_2SO_4+HF
OLEUM
H_2SO_4
FLUORSPAR
ANHYDRITE

Figure 5-2 Process Flowsheet for the Manufacture of Hydrofluoric Acid[3] Using Buss Technology

1. Premixer (Ko-kneader)
2. Rotary kiln
3. Precondenser
4. Primary scrubber
5. 1st condenser
6. 2nd condenser
7. Storage tank
8. Absorption tower (H_2SO_4)
9. 1st weak acid scrubber
10. 2nd weak acid scrubber
11. Storage tank
12. Exhaust fan
13. Rectifying column
14. Distillation column
15. Storage tank

The incorporation of the Ko-Kneader provides a series of important advantages over conventional HF processes, namely:

1. By conducting the first, most corrosive portion of the reaction in a relatively small piece of equipment (about 6-ft. long by 1 ft. in diameter as compared with the 55 by 8 ft. reaction kiln), the initial investment and replacement cost of corrosion-resistant-alloy parts is kept low and the parts are physically easy to replace.
2. The thorough mixing of sulfuric acid and spar accelerates the subsequent reaction in the kiln, increasing plant capacity as much as 30% for a given kiln size.
3. A much smaller excess (or even stoichiometric amounts) of sulfuric acid can be used, since separation of the two components is no longer possible after leaving the Ko-kneader and a local shortage of sulfuric acid is avoided. This results in better quality HF and in an anhydrite quality suitable for further processing.
4. Due to the perfectly homogeneous mixture of sulfuric acid and spar substantially lower temperature can be employed in the kiln, whereby: (a) the sulfuric acid has a lower vapor pressure and contaminates the HF stream to a lesser extent and (b) the kiln is subjected to much less chemical attack.

The other specific feature of the Buss process is that it results in a by-product anhydrite and not in the gypsum pond slurry used in most other processes. Figure 5-3 shows an anhydrate recovery flowsheet.[3]

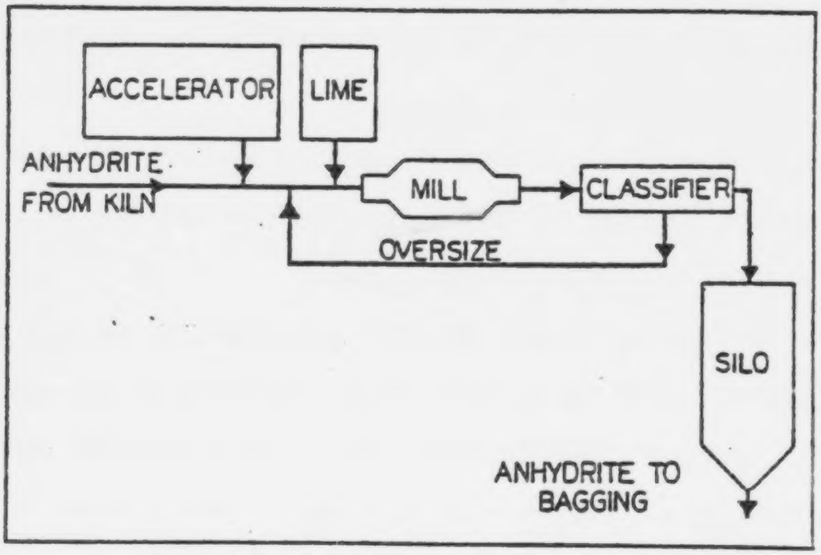
ACCELERATOR
LIME
ANHYDRITE FROM KILN
MILL
CLASSIFIER
OVERSIZE
SILO
ANHYDRITE TO BAGGING

Figure 5-3 Anhydrite Recovery Flowsheet[3]

The anhydrite leaves the kiln through a seal screw. It contains a small amount of unreacted sulfuric acid which is neutralized with lime. An accelerator is added and anhydrite is ground to the standard commercial fineness. The anhydrite can be marketed as a high strength building material or a soil conditioner.

Three plants are believed to use the Buss process.

b. Typical Process[7]

Figure 5-4 shows a schematic of an Exemplary Process used by EPA in the study for effluent limitation guidelines and New Source Performance Standards. It is believed that four or five plants use this process. The flow diagram is similar to that for the Buss Process, major differences being that no premixer is used and that anhydrite is slurried and transported to the gypsum pond. Another difference is that fluosilicic acid is not recovered in this process so lower SiO_2 content can be tolerated in spar. It might also result in SiF_4 emissions. All HF is recovered as anhydrous in both the Exemplary and Buss Process. The tail gas emission volume from this process is considerably lower than that from the Buss Process.

c. Aluminum Fluoride Manufacturing Process

Aluminum fluoride is one of the major products in which HF is used as a raw material. In a typical AlF_3 process gaseous HF emanating from the kiln is contacted directly with hydrated aluminum in a fluidized bed reactor. Some plants use all HF together with impurities for AlF_3 production, while other isolate a portion of gaseous HF as anhydrous using an absorption train similar to that used in a typical process. In the case when all HF is used in gaseous form for AlF_3 production, it is questionable if it can be considered an HF manufacturing plant. In such case only two steps used in a typical HF manufacturing plant, namely spar drying and its reaction with H_2SO_4 in the kiln, are utilized. It is believed that at least three plants utlize this process.

d. Patented Process

In the patented process fluorspar is reacted with a mixture of sulfuric acid, sulfur trioxide, and water vapor at a temperature low enough to allow liquid H_2SO_4 to condense on and to react with CaF_2 but high enough so that CaF_2 particles do not become sticky. The temperature of reaction can be closely controlled and the resulting anhydrite can be readily withdrawn from the reactor. The heat for reaction (between spar and H_2SO_4) is provided through reaction of steam and SO_3. An additional benefit of this process is that the use of heat transfer surfaces and attendant problems has been eliminated.

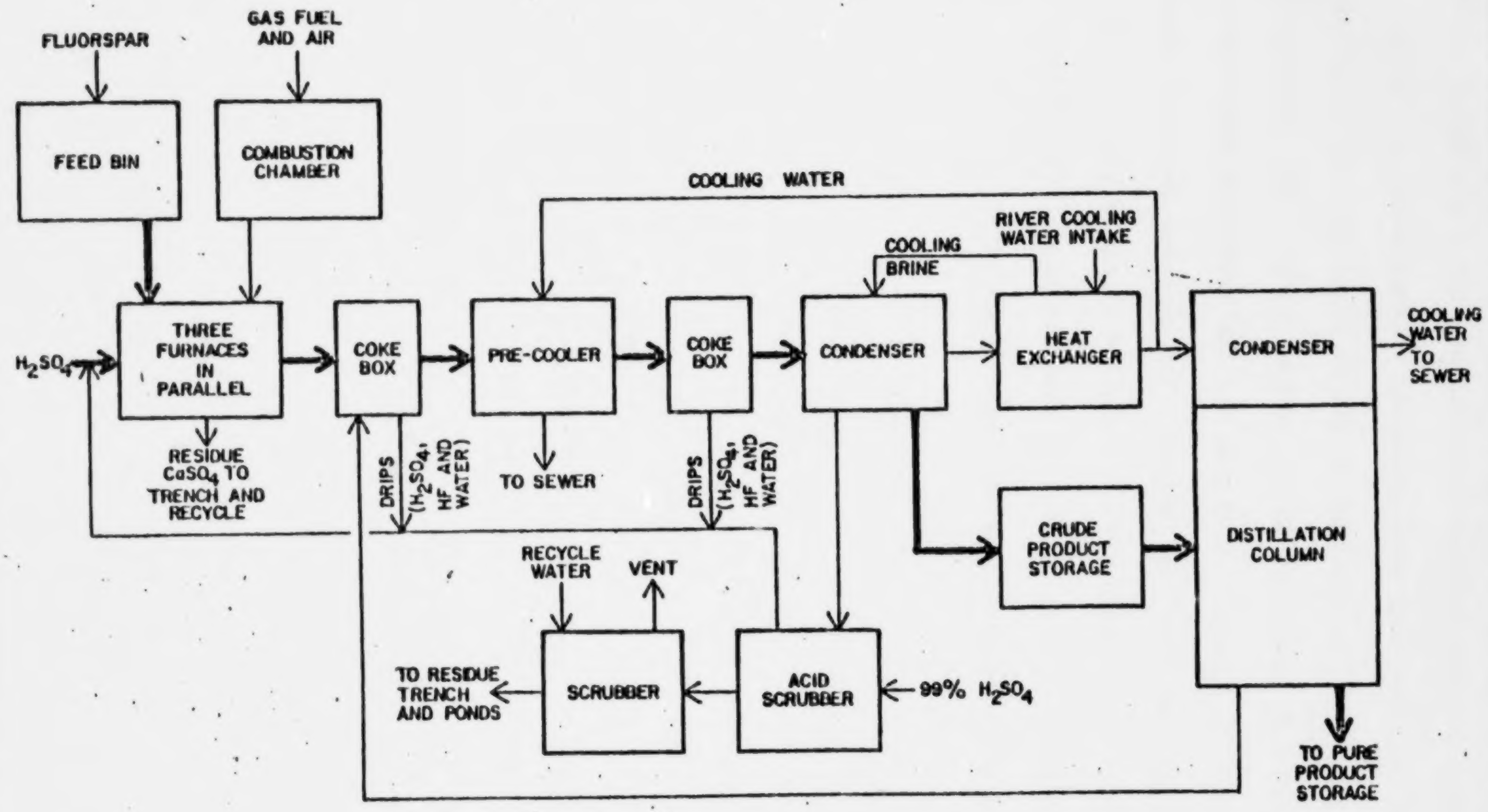
FLUORSPAR
GAS FUEL AND AIR
FEED BIN
COMBUSTION CHAMBER
COOLING WATER
COOLING BRINE
RIVER COOLING WATER INTAKE
H_2SO_4
THREE FURNACES IN PARALLEL
COKE BOX
PRE-COOLER
COKE BOX
CONDENSER
HEAT EXCHANGER
CONDENSER
COOLING WATER TO SEWER
RESIDUE $CaSO_4$ TO TRENCH AND RECYCLE
DRIPS (H_2SO_4, HF AND WATER)
TO SEWER
DRIPS (H_2SO_4, HF AND WATER)
CRUDE PRODUCT STORAGE
DISTILLATION COLUMN
RECYCLE WATER
VENT
TO RESIDUE TRENCH AND PONDS
SCRUBBER
ACID SCRUBBER
99% H_2SO_4
TO PURE PRODUCT STORAGE

FIGURE 5-4[7]

EPA EXEMPLARY HYDROFLUORIC ACID PROCESS FLOW DIAGRAM

5.4 Recovery of Fluoride Value From Phosphate Rock

Most phosphate rock used in the manufacture of phosphate fertilizer contains 3-5% fluorine in the form of the mineral fluorapatite ($Ca_3(PO_4)_3F$). When this rock is treated by either acid or thermal processes, fluorine is released as SiF_4. Many studies to produce HF from this source have been made[9] but two hurdles exist:

1. SiF_4 cannot be conveniently converted into HF.
2. Collection of SiF_4 for an economic capacity is expensive. A proposed process[10] starts by reacting silicon tetrafluoride with recycled ammonium fluoride solution to form ammonium flousilicate.

$$SiF_4 + 2NH_4F \rightarrow (NH_4)_2SiF_6$$

When this solution is neutralized with ammonia, silica precipitates and more ammonium fluoride is formed.

$$(NH_4)_2SiF_6 + 2\ H_2O + 4\ NH_3 \rightarrow SiO_2 + 6\ NH_4F$$

The ammonium fluoride solution (except that recycled) is evaporated to a salt concentration of 94-95%, when some conversion to ammonium bifluoride, NH_4HF_2, takes place by vaporization of ammonia. The evaporation continues until a salt concentration of 98% is reached, when the mixture solidifies at about 100°C. The solid mixture of ammonium fluoride and bifluoride, containing 60% of fluorine, is decomposed with 93-95% sulfuric acid at 180-190°C. Ammonium bisulfate is the principal component of the residue; this can be converted to ammonium sulfate by neutralizing with ammonia.

The economics of this process depend on a low-cost supply of silicon tetrafluoride, a premium market for precipitated silica (proposed, for example, as reinforcing pigment for rubber), and a local market for ammonium sulfate. The process is handicapped by a large filtration and evaporation load.

The alternative way to recover the fluoride value from phosphate rock is to use waste fluosilicic acid. H_2SiF_6 is formed in the phosphate fertilizer plants' scrubber towers in which SiF_4 hydrolyzes:

$$3\ SiF_4 + 2\ H_2O \rightarrow SiO_2 + 2\ H_2\ SiF_6$$

Two procedures to recover HF from $H_2\ SiF_6$ can be used.[11] The first procedure is direct hydrolysis of $H_2\ SiF_6$ according to the following reactions:

$$H_2\ SiF_6 + 2\ H_2O \rightarrow SiO_2 + 6\ HF$$

The reaction is carried out when $H_2\ SiF_6$ is volatilized in a flash vaporizer and the vapors are passed through a quartz tube externally heated to 1000°C. A water cooled copper condenser is used to recover HF.

The results of a laboratory study showed that direct hydrolysis at elevated temperatures was subject to many mechanical difficulties, and that corrosion of construction materials was a serious problem. Elimination of SiO_2 from the HF product was generally poor.

The second procedure, showing more promise, is hydrolysis of lime - neutralized $H_2\ SiF_6$. Neutralization proceeds in two steps:

$$H_2\ SiF_6 + Ca\ (OH)_2 \rightarrow Ca\ SiF_6 + 2\ H_2O$$

$$Ca\ SiF_6 + 2\ Ca\ (OH)_2 \rightarrow 3\ CaF_2 + SiO_2 + 2\ H_2O$$

More SiO_2 is needed to satisfy the following reaction:

$$CaF_2 + SiO_2 + H_2O \rightarrow Ca\ SiO_3 + 2\ HF$$

The apparatus used for hydrolysis of lime - neutralized $H_2\ SiF_6$ is shown in Figure 5-5.[11]

To operate the system, a charge of 2 1/2 to 3 kilograms of pellets is placed in the reactor tube, forming a bed about 16 to 20 inches deep in the zone of maximum heat. The reactor and flash vaporizer are brought up to temperature; the vaporizer is heated to 450°C and the reactor heated,

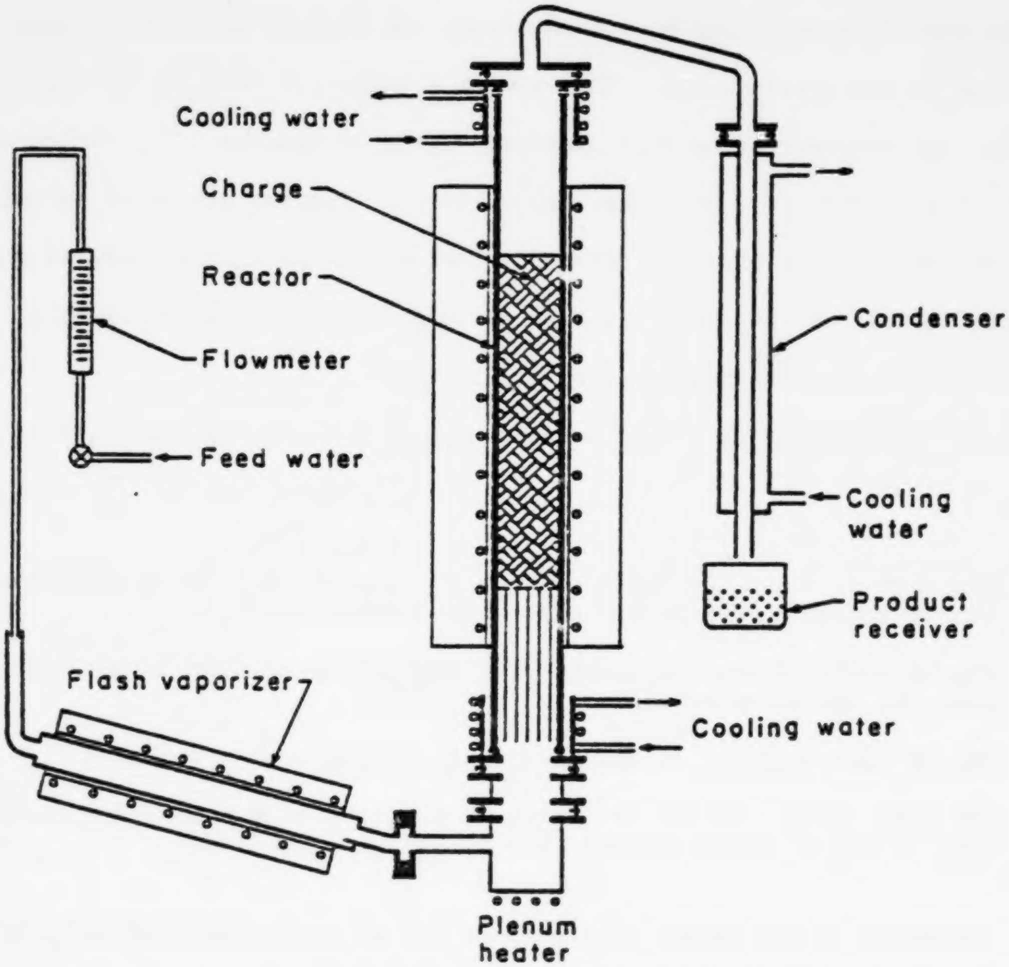
Cooling water
Charge
Reactor
Flowmeter
Feed water
Condenser
Cooling water
Product receiver
Flash vaporizer
Cooling water
Plenum heater

FIGURE 5-5 - Vertical Hydrolysis System[11]

for most of the tests, to 1,000°C, measured at the outside surface of the reactor tube. When operating temperatures are attained, the flow of water was started to the vaporizer at the desired rate. This causes a temporary drop in the vaporizer temperature, but recovery is usually complete within 15 minutes. The condensed HF product is collected in a polyethylene container. Samples are taken periodically and analyzed for fluorine and SiO_2 content. The test is usually terminated when 80 to 90 percent of the available fluorine has been removed from the reactor charge and the solution becomes increasingly dilute.

Reaction characteristics of steam-hydrolysis of lime-neutralized H_2 SiF_5 are as follows:

1. Addition of 70 to 100 percent of the calculated SiO_2 requirement has little effect on hydrolysis rate or HF concentration.
2. The HF concentration increases with increasing reaction temperature over the investigated range 950° to 1,100°C.
3. The HF concentration increases with decreasing water feed rate.
4. The SiO_2 content of the condensed HF product does not exceed 1.8 percent of the fluoride content, and is usually much lower.

The conclusion of the survey of processes for HF production from phosphate rock is that they are still in the early stages of development. It will probably take decades before such processes can be developed into a full scale production. HF manufacturing e from spar will probably remain the most economical process for years to come.

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10. Boguslavskiy, S.N., etal, Khim Prom, 1961 (7), 6-8.
11. Good, P.C., Tress, J.E., Recovery of Hydrofluoric Acid for Waste Fluosilicic Acid, Bureau of Mines Report of Inv. 7213, 1968, 14 p.

6.0 EMISSION SOURCES AND RATES IN HF PRODUCTION AND MANUFACTURING

6.1 Sources and Nature of Point Source and Fugitive Emissions

There are very few sources of air emissions in a HF manufacturing plant. The major sources and pollutants can be divided into three categories:

1. Spar drying and handling

   Spar is received by barges and tank cars and is unloaded into storage areas or silos. In addition to the main storage silo(s), most plants have a separate spar use silo which normally contains one day's supply. Spar unloading results in fugitive emissions which can be substantial under windy conditions. If spar is stored outdoors in a stack, this is a potential source of fugitive emissions.

   The main emission of spar occurs during the spar drying. The gas volumetric flow rate from the dryer is in the order of 2,000-13,000 ACFM. The emission consists of spar as a fine particulate and combustion gases since the rotary kiln dryers are most frequently internally fired. Both natural gas and No. 2 fuel oil are used for firing so that SO_2, NO_x, and CO can be present in the emission stream. The emissions from the dryer are controlled with bag filters; only one plant uses a high energy Venturi scrubber. Dry spar is stored in silo(s) which are, as a rule, also controlled with a bag filter, frequently the same one used for control of the dryer.

2. HF manufacturing

   Almost all HF-producing facilities have only one point source from HF manufacturing (consisting of kiln and absorption train). Since the potential pollutant HF is the desired product, it is in the best interest of the plant to recover all HF. Consequently, HF gas is precooled, removed in refrigerant cooler, treated with sulfuric acid, and finally scrubbed with water. The emissions in the tail gas (after the final scrubber) contain small quantities of HF, SiF_4, and SO_2. The amounts of these compounds depends on the process and its variation.

   a. Buss Process

      In this process, a caustic scrubber is usually employed as a final control step. Since fluosilicic acid is recovered in this process, most of the SiF_4 is removed before entering the final scrubber. Caustic should have 99% efficiency in removing HF.

b. EPA Exemplary Process

The process described as the EPA Exemplary Process uses different scrubbing media in a final scrubber. Depending on whether the scrubber liquid is acidic gypsum pond water, plain water or caustic solution, the efficiency can vary from 70% to 99%. Since fluosilicic acid is not, as a rule, recovered in this process, SiF_4 may be a major pollutant. The emissions might be particularly high when acid scrubbing is used and when spar contains high percentages of SiO_2 (over 0.5%) The tail gas volumetric flow rate in this process is smaller than in the Buss Process and runs in the order of hundreds of ACFM. A typical tail gas exhaust stack is shown in Figure 6-1. There is a possibility of HF emissions from acidic pond water; this will be discussed under water pollution in Section 6.4. The emissions from spar handling and drying are similar to those from the Buss Process.

c. AlF_3 Manufacturing Process

There is no tail gas in this process if all HF is used for AlF_3 production in a fluidized bed reactor. When HF isolation is used, emissions are similar to those from the Exemplary Process. Spar handling and drying emissions are similar to those described for the other processes.

d. Patented Process

In this process the tail gas is scrubbed with limed water, so low HF emissions are expected. SiF_4 emissions could be high since fluosilicic acid is not recovered. SO_2 content in the tail gas could be high because of SO_2 evolution in the reactor. Spar handling and drying emissions do not vary from the other processes.

In addition to tail gases, reaction kilns are potential sources of HF emissions. Normally the kiln operates under negative pressure but, under upset conditions caused by a plugged absorption train or incorrect spar-H_2SO_4 ratio, it can emit HF. Many plants have an emergency scrubber or a bypass to the final scrubber which is operated under upset conditions.

3. HF Handling and Other Fugitive Sources

Almost all HF isolated in manufacturing is in the anhydrous form. If 70% is the desired product, it is obtained by mixing anhydrous HF with water. The HF emissions from this source are frequently controlled by a wet scrubber using pure water as a scrubbing liquid.

Anhydrous and aqueous HF is stored in the storage vessels and transferred to tank cars or trucks for transportation. If not properly controlled, the loading process is a possible source of fugitive emissions. At least one plant was found where this was a major source of intermittent HF emissions causing complaints from the neighbors.

Leaks throughout the HF plant can be another source of fugitive emissions caused by the corrosive nature of HF. HF plants have an unusually high ratio of maintenance to operating personnel and good maintenance was pointed out as a key to successful HF manufacturing.

A significant unknown in HF plant air emissions is the gypsum pond. In cases when pond liquid is acidic, it could be a source of fugitive HF and SiF_4 emissions.

6.2 Controlled and Uncontrolled Emission Rates

As a first step in the determination of emission rates from HF manufacturing, TRC obtained printouts for all eleven HF manufacturing facilities in the National Emission Data System (NEDS) and the Compliance Data System (CDS). Both computerized data bases were of little help in this project. NEDS contains little quantitative data most of which is out of date and unreliable. Most quantitative information is listed as confidential and cannot be presented in this report. CDS contained no quantitative information.

Figure 6-2[1] shows a schematic of HF manufacturing indicating major emission streams and emission rates. This process model assumes that the only HF fluoride emission stream is tail gas. No spar emissions from the dryers have been estimated in this model but another study[5] indicates that maximum emissions after control would not exceed 20 lb/ton. The emission factor ranking shown in Table 6-1 is relatively low indicating that these factors must be considered questionable.

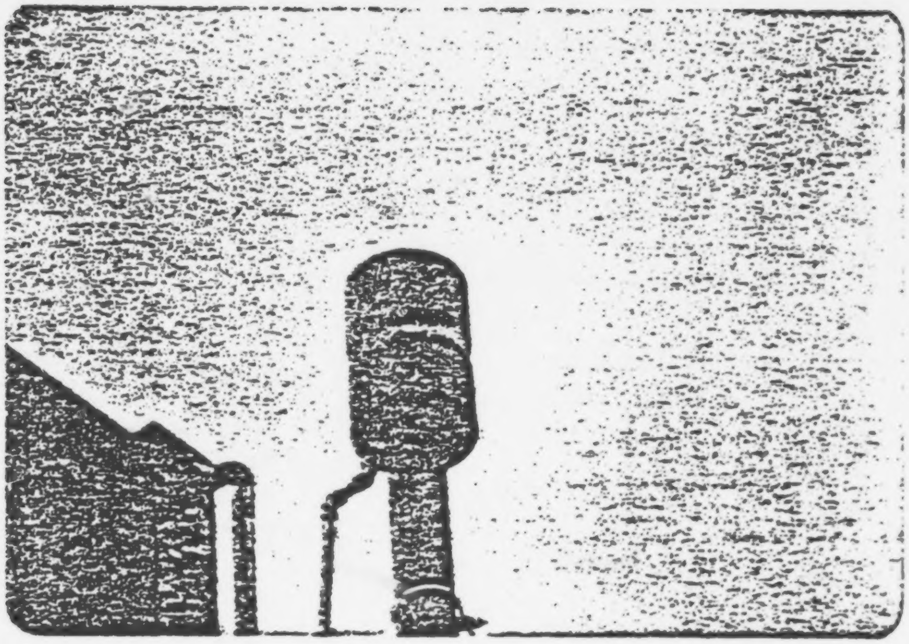

Figure 6-1: Typical Tail Gas Exhaust Stack

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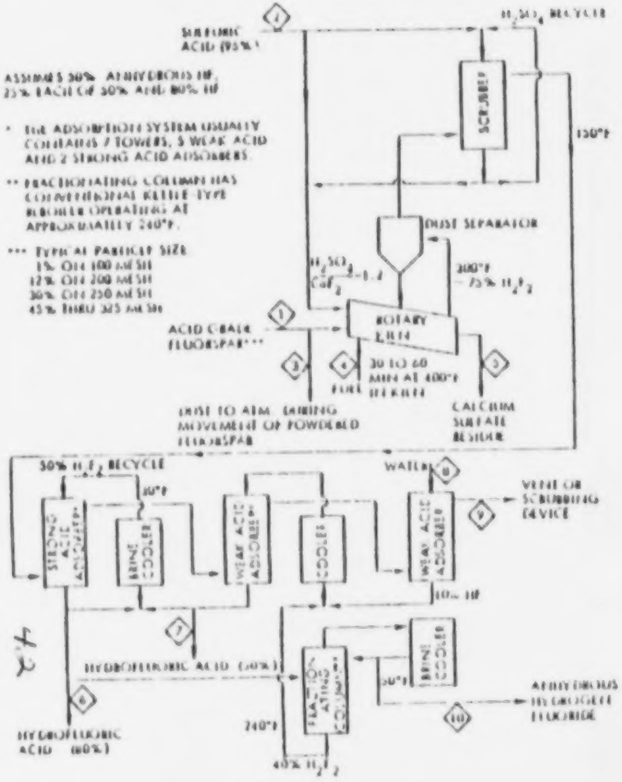
best available copy.


ASSUMES 50% ANHYDROUS HF, 25% EACH OF 50% AND 80% HF
* THE ADSORPTION SYSTEM USUALLY CONTAINS 7 TOWERS, 5 WEAK ACID AND 2 STRONG ACID ADSORBERS.
** FRACTIONATING COLUMN HAS CONVENTIONAL KETTLE-TYPE REBOILER OPERATING AT APPROXIMATELY 240°F.
*** TYPICAL PARTICLE SIZE
1% ON 100 MESH
12% ON 200 MESH
30% ON 250 MESH
43% THRU 325 MESH
SULFURIC ACID (95%)
2
H2SO4 RECYCLE
SCRUBBER
150°F
DUST SEPARATOR
H2SO4 / CaF2 = 1.2
300°F
~75% H2F2
1
ACID GRADE FLUORSPAR***
ROTARY KILN
3
4
FUEL
30 TO 60 MIN AT 400°F IN KILN
5
DUST TO ATM. DURING MOVEMENT OF POWDERED FLUORSPAR
CALCIUM SULFATE RESIDUE
50% H2F2 RECYCLE
30°F
STRONG ACID ADSORBER*
BRINE COOLER
WEAK ACID ADSORBER*
COOLER
WEAK ACID ADSORBER*
WATER
8
VENT OR SCRUBBING DEVICE
9
10% HF
7
HYDROFLUORIC ACID (60%)
FRACTIONATING COLUMN**
BRINE COOLER
30°F
ANHYDROUS HYDROGEN FLUORIDE
10
240°F
40% H2F2
6
HYDROFLUORIC ACID (80%)

4.2

BASES - 25 TONS/DAY HF PRODUCTION (ASSUMES 50% ANHYDROUS HF, 25% EACH OF 50% AND 80% HF)

PROCESS STREAMS - LBS/HR

Material	Stream Numbers									
	1	2	3	4	5(B)	6	7	8	9*	10
HF						510 (l)	510 (l)		26 (g)(B)	1010(l)
SiF_4									34 (g)(D)	
CaF_2	4100(s)(C)		20(s)(D)		40(s)(C)					
Total Fluorides	4100		20		40	510	510		60	1010
Total as F	2000		10		20	400	400		50	960
$CaCO_3$	40(A)									
SiO_2	40(A)				20					
S	2(A)									
H_2SO_4 (98%)		5400								
$CaSO_4$					7100					
CO_2									16(g)	
SO_2										
H_2O	4(A)					130	510	400	3(g)	
Fuel				7×10^6 BTU						
Approx. Total Stream	4200	5400	20	--	7100	640	1000	400	60	1010

*Gaseous effluent stream

(A) Impurities in the fluorspar feed.

(B) The calcium sulfate residue stream may liberate fluorides. Literature search revealed no data.

(C) References 2, 3

(D) Reference 4

Soluble fluoride evolution factor = 52 lb F/ton HF

(s) Solid

(g) Gaseous

Figure 6-2: Hydrofluoric Acid Production - Uncontrolled Process Model[1]

TABLE 6-1

EMISSION FACTOR RANKING FOR HYDROFLUORIC ACID[4]

Emission Data	Process Data	Engineering Analysis	Total
0-20	0-10	0-10	
3	5	3	11

The soluble fluoride emission evaluation factor is 52 lb F/ton HF. It must be mentioned here that there are problems in evaluating fluoride emissions by available sampling methods. If Method 13 is used as a means of determining fluoride emissions, both gaseous and solid fluorides would be measured. It appears that any evaluation of fluoride emissions should also include the spar stream.

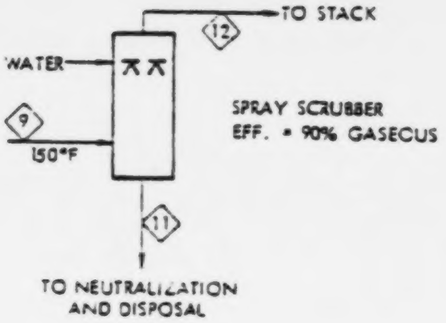
Figure 6-3 shows the controlled process model in which the tail gas is scrubbed. The soluble fluoride emission is estimated to be 4.1 lb F/ton HF.

Fugitive emissions have not been estimated but indications are they might be high. The State of Louisiana regulatory agency Emission Inventory Questionnaire shows that fluoride fugitive emissions are of the same order of magnitude as controlled ones. One indication of fugitive emissions is ambient fluoride concentration. The Texas Air Control Board sampled HF property line ground levels at one location and discovered that plant downwind HF concentration is 2-10 ppb higher than upwind.

6.3 Annual Emission Rates and Plant Inventories

Table 6-2 shows the annual estimated soluble fluoride emissions from HF production. The basis for calculations is available emission factors and an expected annual growth rate of 6%. This projected growth rate is undoubtedly much too high since the production capacity for 1977 is about the same as it was in 1970. The projected production for the year 1982 obtained from industry shows that no growth is expected.

Table 6-3 shows the emission inventory for HF manufacturing plants. An attempt was made to develop emission factors based on a plant's emission inventory but data are too scarce, variable, and are too unreliable to draw valuable conclusions.


TO STACK
12
WATER
9
150°F
SPRAY SCRUBBER
EFF. = 90% GASEOUS
11
TO NEUTRALIZATION
AND DISPOSAL

BASIS - 25 TONS/DAY HF PRODUCTION
(ASSUMES 1/2 ANHYDROUS HF, 1/4 50% HF AND 1/4 80% HF PRODUCED)

PROCESS STREAMS - LB/HR

Materials	Stream Number		
	9	11	12*
HF	26(g)	24(g)	2(g) (Est.)
SiF_4	34(g)	31(g)	3(g) (Est.)
Total Fluorides	60	55	5
Total as F	50	46	4
CO_2	16(g)		16(g)
H_2O	3(g)	2.5 (al)(A)	0.5(g)
Approx. Total Stream	80	60(A)	20

*Gaseous Effluent Stream

(A) Plus scrubbing water.

(B) Assumes 100% usage of scrubbers on all facilities.

Source	Soluble Fluoride Emission Factor - lb F/ton HF
Scrubber	4.1
Assumed Fugitive	0.0
Total Emission	4.1

Overall soluble fluoride emission = 4.1 lb F/ton HF(B)

Figure 6-3: HF Production - Controlled Process Model[1]

TABLE 6-2

SOLUBLE FLUORIDE EMISSIONS FROM HF PRODUCTION[1]
(Based upon a 6% annual growth factor)

	1970	2000
HF Production (10^6 tons/year)	0.34	2.60
Soluble Fluoride Evolution Factor (lb F/ton HF)	52	52
Soluble Fluoride Emission Factor with Current Practice (lb F/ton HF)	4.1	4.1
Soluble Fluoride Emission Factor with 99% Control (lb F/ton HF)	--	0.52
Soluble Fluoride Evolution (10^3 tons F/year)	8.84	67.6
Soluble Fluoride Emission with Current Practice (10^3 ton F/year)	0.70	5.33
Soluble Fluoride Emission with 99% Control 10^3 ton F/year)	--	0.68

TABLE 6-3

EMISSION INVENTORY FOR HF MANUFACTURING PLANTS

Plant	Location	Capacity 1975 Date Thousand Tons	Emission Source	Control	ACFM	Emission Rate lb/hr	Pollutant	Efficiency %
Allied	Nitro	15	Spar dryer	Baghouse	5,000	4	Spar	99
	WV		Tail gas	Wet scrubber		-		99
	Pittsburg	12	Spar unload	Baghouse	160	0.01	Spar	99.9
	CA		Soda ash unload	Wet scrubber	-	120	Soda ash	96
	Geismar	45	Spar silo	Baghouse	1,600	21	Spar	99
	LA		Tail gas	Scrubber	170	0.6	SO_2	
						0.8	HF	96-99
			Spar use silo	Baghouse	1,600	21	Spar	96-99
	Baton Rouge	20	Spar dryer	Baghouse	8,900	6.5	Spar	99
	LA		Spar silo	Baghouse	85	0.1	Spar	99
			Tail gas	Wet scrubber	750	0.8	SiF_4	-
						1.8	SO_2	
Dupont	LaPorte	100	Spar silo	Baghouse	-	15	Spar	99
	TX		Tail gas	Scrubber		6.9	SO_2	
						0.3	F	
Alcoa	Point Comfort	55	Spar dryer	Baghouse	3,787			
	TX		Spar silo	Baghouse	1,836			
Stauffer	Greens Bayou	18	-	-	-	-	-	-
	TX							
Kaiser	Gramercy	50	Spar loading			2.8	Spar	
	LA		Spar fugitive			7.5	Spar	
			Blower fugitive			2.6	HF	
			4 generators fugitive			3.6	F	
			Spar dryer	Baghouse	13,220	5.3	Spar	99
						0.8	NO_x	
			Spar silo	Baghouse	1,260	0.8	Spar	99
Pennwalt	Calvert City	25	Spar unloading	-	-	-	-	-
	KY							
Essex	Paulsboro	11	Spar dryer	Baghouse	9,000	0.8	Spar	99
	NJ		Ball mill	Baghouse	-	0.5	Spar	99
			HF kiln	-	-	0.5	HF	
Harshaw	Cleveland	18	Spar dryer	Baghouse	3,000	10	Spar	99.5
	OH		Tail gas	Scrubber	4,750		F	95

In conclusion, an emission of 20 lb/ton of spar is realistic and in line with findings during plant visits and contacts with the industry. An emission of 4 lb/ton of soluble fluorides also appears to be realistic.

6.4 Gypsum Pond Emissions

Most HF manufacturers slurry anhydrite and transfer it to gypsum ponds. The gypsum ponds have been investigated in the phosphate fertilizer industry and were found to be a significant source of fluoride emissions and a source of radioactive isotopes which can be leached into aquifers. Figure 6-4 shows the wastewater recycling used in an EPA Exemplary Plant[6] where all process and scrubber wastewaters are recycled. The waters used to slurry and remove anhydrite and scrubber water are fed to a pond system after being treated with caustic or soda ash and lime to precipitate fluorides and adjust the pH. In the pond system, the insolubles are settled out and waters are then reused.

Table 6-4 shows waste products from HF manufacturing at the Exemplary Plant. Only cooling water is discharged from this facility. Neutralization of sulfuric and hydrofluoric acid wastes with lime, followed by removal of precipitated $CaSO_4$ and CaF_2 in settling ponds, reduces fluorides to 18 mg/l and calcium sulfate to approximately 2,000 mg/l in treated water streams. Lime treatment of the isolated wastes and settling pond removal of precipitate reduces the fluorine content of this small stream to approximately 10 mg/l. No fluoride emission is expected from the gypsum ponds which are neutralized to pH 6-7. However, contacts with HF manufacturing plants indicates that some ponds have a pH of 1. In that case, HF and SiF_4 emission is possible. Measurement of fluoride emission rate is recommended.

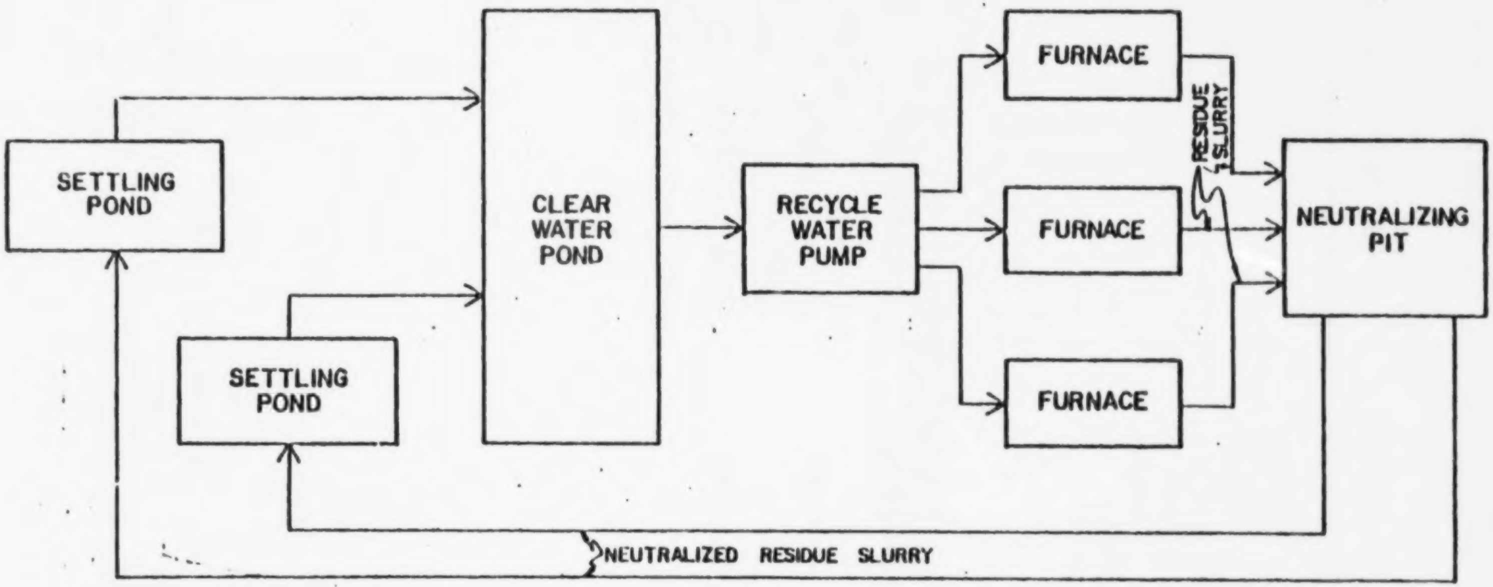

SETTLING POND
SETTLING POND
CLEAR WATER POND
RECYCLE WATER PUMP
FURNACE
FURNACE
FURNACE
RESIDUE SLURRY
NEUTRALIZING PIT
NEUTRALIZED RESIDUE SLURRY

Figure 6-4: Effluent Recycle System at an Exemplary Plant[6]

TABLE 6-4

WASTE PRODUCTS FROM HF MANUFACTURING PLANTS[6]
(Based on Estimates for the EPA Exemplary Plant)

Waste Product Product	Process Source	Avg. kg/kkg (lb/ton)
1. $CaSO_4$	Kiln (reactor)	3,620 (7,240)
2. H_2SO_4	Kiln (reactor)	110 (220)
3. CaF_2	Kiln (reactor)	63 (126)
4. HF	Kiln (reactor)	1.5 (3)
5. H_2SiF_6	Scrubber	12.5 (25)
6. SiO_2	Kiln (reactor)	12.5 (25)
7. SO_2	Scrubber	5 (10)
8. HF	Scrubber	1 (2)

	Total Quantity		
Type	cu m/day (gpd)	l/kkg(gal/ton)	Recycled
Cooling (river water)	3,270 (864,000)	90,140 (21,600)	0 percent
Slurry and Scrubber	3,270 (864,000)	90,140 (21,600)	100 percent

6.5 References

1. Robinson, J.M., et al., Engineering and Cost Effectiveness Study of Fluoride Emissions Control, p. 3-297, Vol. 1. February 1972, NTIS No. PB 207 506.

2. Kirk-Othmer, Encyclopedia of Chemical Technology, Interscient Publishers, New York 1965, Vol. 9.

3. Gaith, W.L., Industrial Chemicals, J. Wiley and Sons, Inc., 3rd Ed., 1965.

4. TRW Systems Group, Air Pollutant Emission Factors, Dept. of HEW, Contract No. 22-69-119, NTIS No. PB 206-924, April 1970.

5. Rogers, W.R., Muller, K., Hydrofluoric Acid Manufacture, Chemical Engineering Program 59:85-88, May 1963.

6. Martin, E.E., Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Inorganic Products Segment of the Inorganic Chemicals Manufacturing Point Source, EPA Report 440/1-74-007a, NTIS No. PB 238-611.

7.0 CONTROL OF EMISSIONS FROM HF MANUFACTURE

Emissions from HF manufacture can be divided into three categories:

1. Particulate emissions from spar handling and drying
2. Gaseous emissions from the HF absorption train (tail gas)
3. Fugitive emissions from process, HF loading, and gypsum pond.

7.1 Particulate Emission Control

The largest source of particulate emission in HF manufacture is the spar dryer. The secondary sources of spar are storage silos and transport of solid materials. These emissions can be controlled with wet or dry gas cleaning devices. Table 7-1 shows the advantages and disadvantages of both methods as applied to a broad range of particulate matter.

Out of 9 plants, 8 are using the dry method applying cyclones and baghouses. A typical baghouse used in a HF manufacturing plant is shown in Figure 7-1.

Figure 7-2 shows a typical baghouse with pulsed air cleaning frequently used in spar emission control.

In selecting the baghouse for spar control, the major parameter is air to cloth ratio.

Figure 7-3 shows a kiln venturi scrubber system similar to one that can be used on a spar dryer. In the selection of the wet scrubber for particulate control, one should consider the following factors[4]:

1. Particulate characteristics: physico-chemical properties
2. Carrier gas characteristics: temperature, pressure, humidity, etc.
3. Process factors: gas flow rate, particulate concentration, pressure drop, etc.
4. Operational factors: floor space, materials of construction.

TABLE 7-1

ADVANTAGES & DISADVANTAGES OF WET & DRY AIR & GAS CLEANING DEVICES[1]

ADVANTAGES:

DRY	WET
1. Recover product dry	1. Gases & particles collected together
2. Freedom from corrosion	2. Soluble materials may be readily collected
3. Less storage capacity required for waste	3. High temperature gases cooled
4. Insoluble materials > 0.05 μm may be collected with high efficiency	4. Corrosive gases and mists may be neutralized
5. Recirculation of treated gas may be possible if the gas is respirable.	5. Eliminate fire or explosion hazard.

DISADVANTAGES:

DRY	WET
1. Hygroscopic materials may cake	1. May require recrystallization for soluble particles
2. Dust exposure to maintenance personnel	2. Easily pumped but may need sludge pond
3. High temperature; costly construction	3. Dissoluble particle recovery requires liquid filter
4. Not tolerate acids or corrosive mists	4. Particles < 1μm not easily collected
5. Secondary dust disposal problem	5. Freezing problems
	6. Liquid entrainment in effluent frequent problem
	7. Cleaned air may not be suitable for recirculation, high dewpoint causes condition.

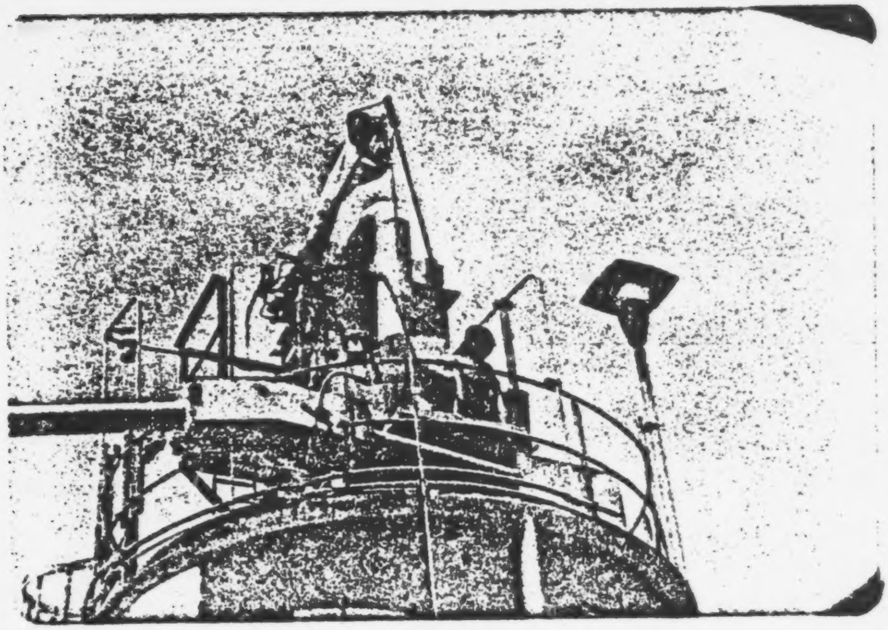


Figure 7-1: Baghouse for Control of Spar Emission

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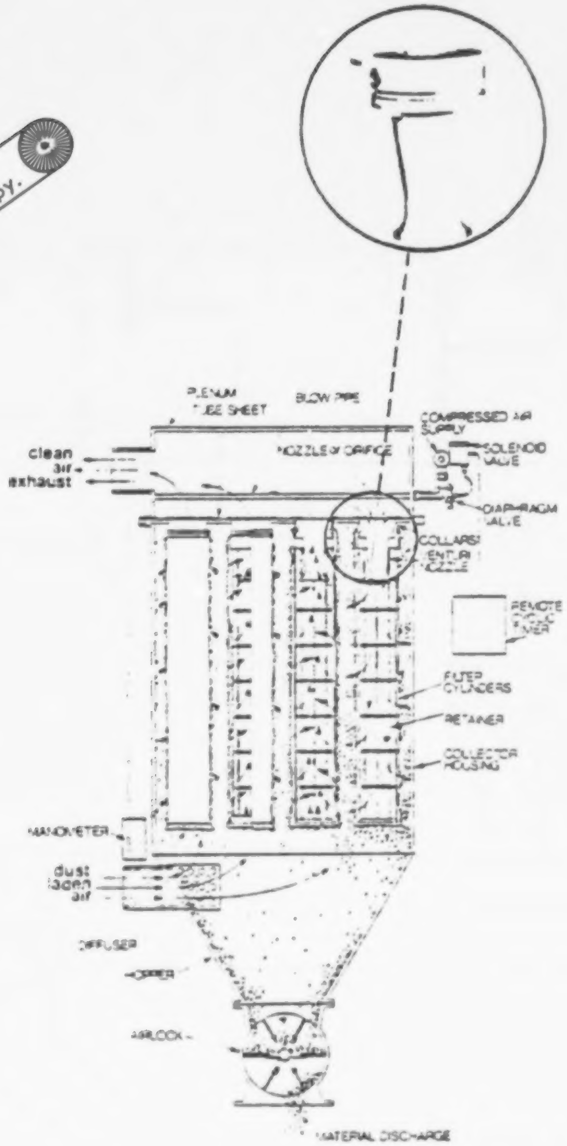
PLENUM
TUBE SHEET
BLOW PIPE
COMPRESSED AIR SUPPLY
clean air exhaust
NOZZLE or ORIFICE
SOLENOID VALVE
DIAPHRAGM VALVE
COLLARS/ VENTURI NOZZLE
REMOTE CYCLIC TIMER
FILTER CYLINDERS
RETAINER
COLLECTOR HOUSING
MANOMETER
dust laden air
DIFFUSER
HOPPER
AIRLOCK
MATERIAL DISCHARGE

Figure 7-2: Typical Baghouse with Pulsed Air Cleaning[1]

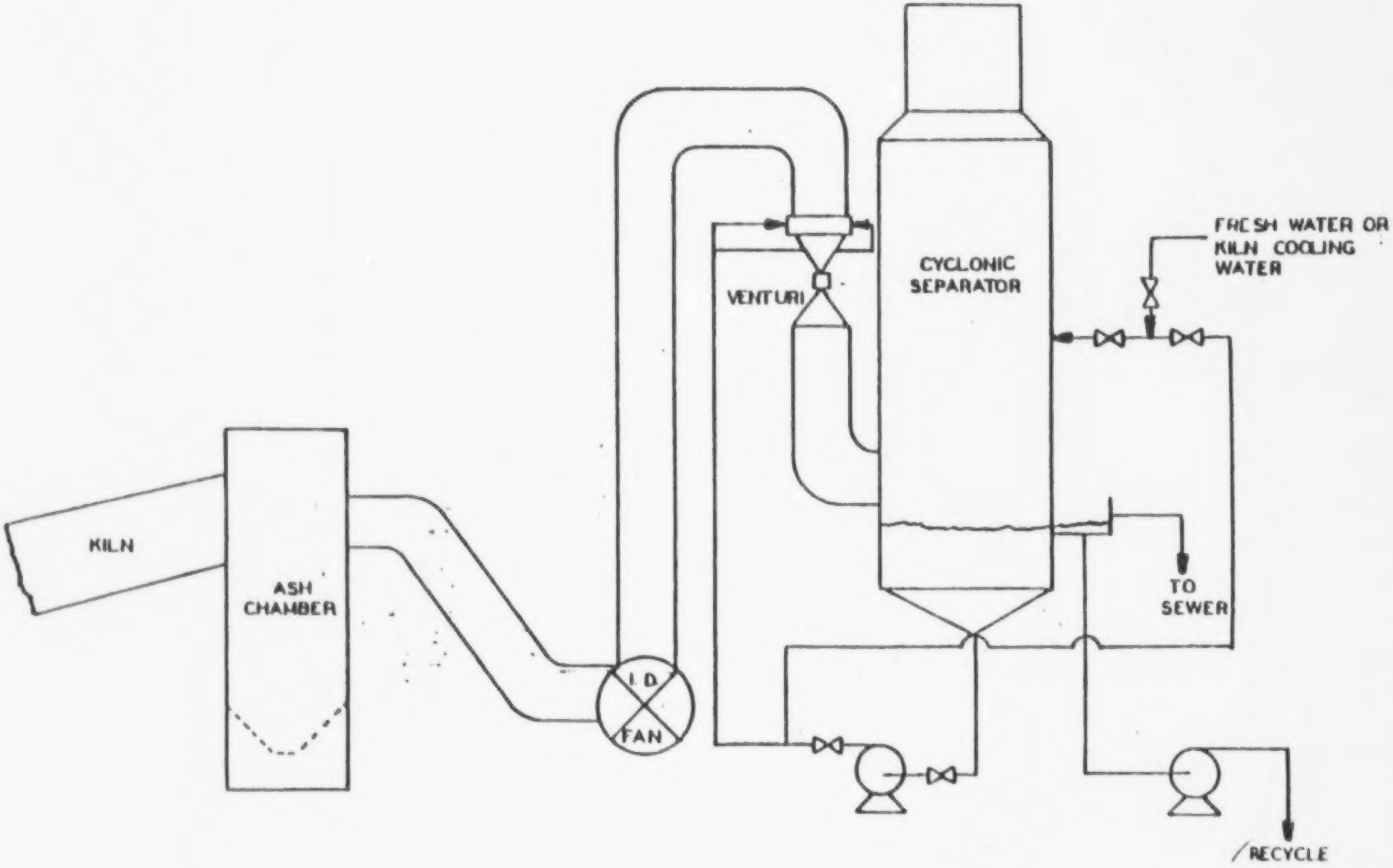
KILN
ASH CHAMBER
I.D. FAN
VENTURI
CYCLONIC SEPARATOR
FRESH WATER OR KILN COOLING WATER
TO SEWER
/RECYCLE

Figure 7-3: Kiln Venturi Scrubber System[3]

Figure 7-4 shows the relationship between collection efficiency and particle size in Venturi scrubber.

Only one HF manufacturing plant uses a high energy Venturi scrubber for spar control.

The review of control technology for spar emission shows that best control technology is the use of fabric filters. The efficiency of fabric filters used in spar control is about 99%. A high energy Venturi with a pressure drop of 20-40 in WG would have a comparable efficiency. The drawback of scrubbers is that they do not recover spar in usable form and create wastewater problems.

7.2 Gaseous Emission Control

The major source of gaseous emission from HF manufacture is tail gas from the absorption train. The major pollutants are HF, SiF_4 and SO_2. The best technique for control of these gaseous pollutants is absorption.

The absorption of tail gas is usually accomplished in a packed tower shown in Figure 7-5. The tail gas is contacted with scrubbing liquid in a counter current fashion. To increase the mass transfer the tower is filled with packing. The gas on its way from bulk gas to bulk liquid and to final elimination has to overcome three resistances[5]:

1. Diffusion through gas phase film
2. Diffusion through liquid phase film
3. Chemical reaction rate.

Any one or a combination of the three resistances can be the rate controlling step. Because of the great solubility of HF and SiF_4 in water, the gas film resistance would be expected to be controlling.

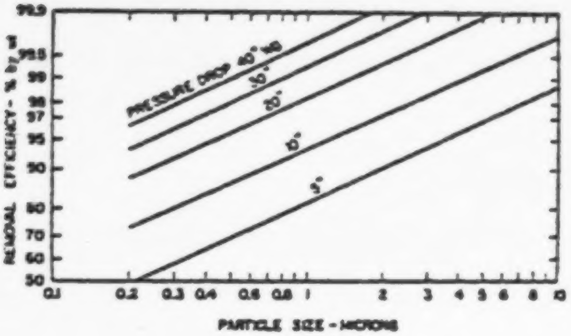

Figure 7-4: Relationship Between Collection Efficiency and Particle Size in Venturi Scrubbers

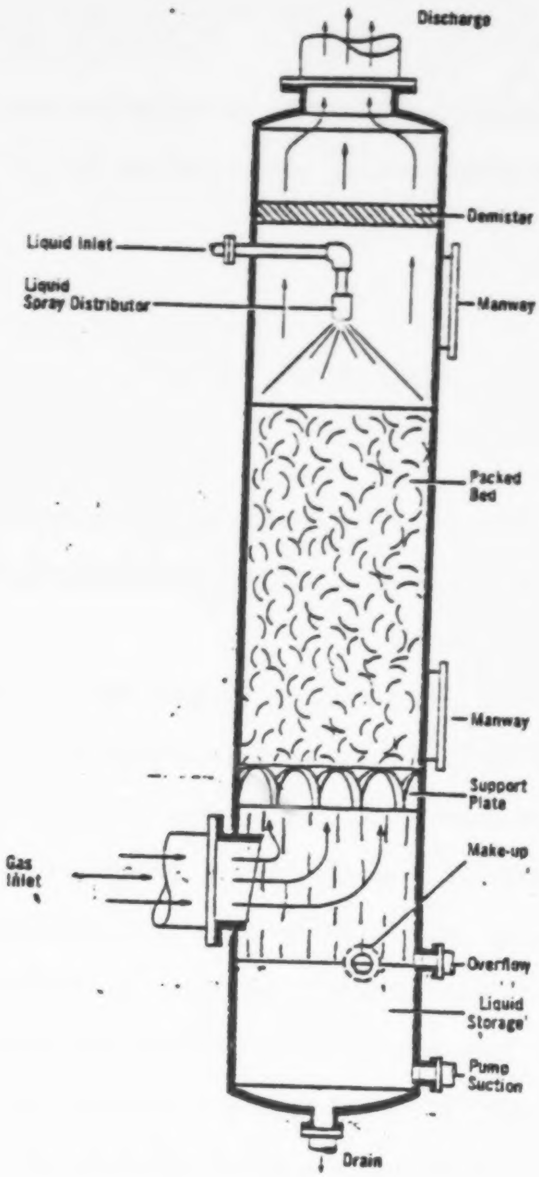
Discharge
Demister
Liquid Inlet
Liquid Spray Distributor
Manway
Packed Bed
Manway
Support Plate
Make-up
Gas Inlet
Overflow
Liquid Storage
Pump Suction
Drain

Figure 7-5: Typical Packed Tower[3]

In such cases and with packed towers, it is usually found that[6]:

$$Kg \sim G^{0.8}$$

Where Kga = mass transfer coefficient, lb moles/(hr)(cu ft)(atm)

G = gas mass flow rate, lb moles/(hr)(sq ft)

Therefore,

$$N_T \sim \frac{Z}{G^{0.2}}$$

where N_T = number of transfer units

Z = tower height, ft

Thus, the number of transfer units obtainable would be controlled by the height of the tower. However, the number of transfer units usually increases as the liquid mass flow rate is increased.

Table 7-2 shows HF absorption data in various wet scrubbers.[6] An important consideration in pollutant removal is the performance of equipment. It is sometimes difficult to compare the performance of two basically different types of equipment in terms of mass flow rates, height of transfer unit or mass transfer coefficients. The performance of equipment has been studied in terms of the number of transfer units. The effect of liquid and gas flow rates is expressed in terms of theoretical power consumed per unit of gas flow rate, as power consumption as such is usually of more economic concern than liquid or gas mass flow rate. Such relations are mainly a matter of convenience and do not necessarily have a theoretical basis. Figure 7-6, 7-7 and 7-8[6] show the relationship between number of transfer units and power consumption in absorption of HF, SiF_4, and SO_2.

Installation	Type of Equipment	Absorbing Liquor	G, Lb./(Hr.)(Sq. Ft.)	L, Lb./(Hr.)(Sq. Ft.)	P_e, Hp., /M Cu. Feet/Min.	P_t, Hp., /M Cu. Feet/Min.	K_ga Lb. Mole (Hr.)(Cu. Ft.)(Atm.)	N_T
A	Cross flow spray	Water	2,110	72	~0.0067	0.0089	~11	~0.33
			1,880	72	~0.0056	0.0098	~12	~0.38
			2,080	103	~0.0067	0.0067	~12	~0.25
			1,830	84	~0.0067	0.017	~15	~0.62
			1,400	92	~0.0061	0.017	~25	~1.00
B	Cross flow spray	Lime water	2,050	105	~0.006	0.013	~35	~1.50
C	Counterflow spray	Water	2,000	800	~0.2	0.10	9	~5.85
D	Parallel flow spray	Lime water	13,800	3,800	~0.23	0.017	51	2.58
E	Counterflow spray	Water	2,000	380	0.24	0.02	~4.3	2.5
F	Venturi	Water	76,000*	42,000*	4.7	0.071	...	2.9
G	Venturi	Water	~70,000*	~40,000–65,000*	2.1	0.074	...	2.0
					2.4	0.11	...	2.7
					2.9	0.071	...	2.3
					3.5	0.095	...	3.0
					4.0	0.12	...	3.9
					4.5	0.13	...	2.3

* Based on throat cross section.

Table 7-2: Hydrogen Fluoride Absorption Data

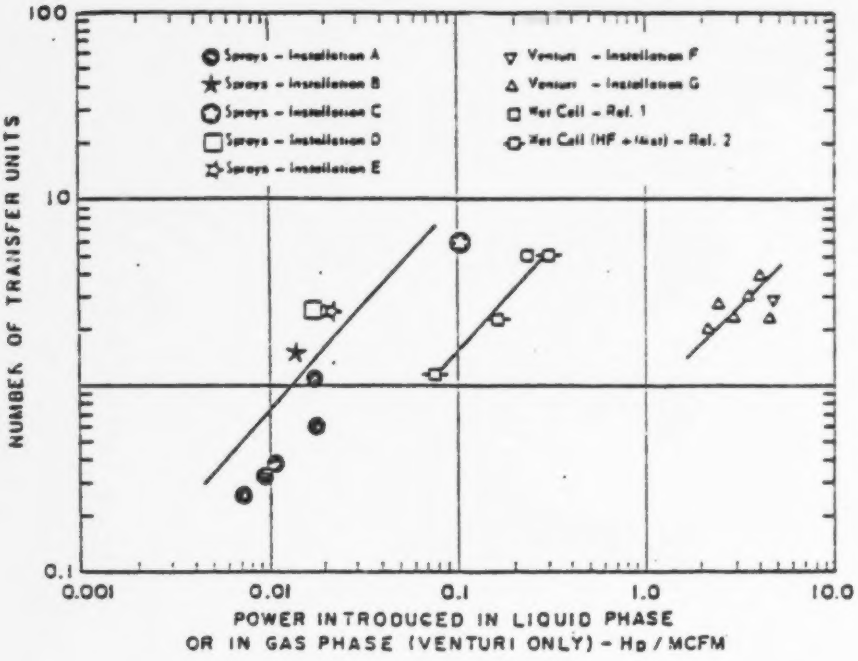

Figure 7-6: Power Consumed in HF Absorption

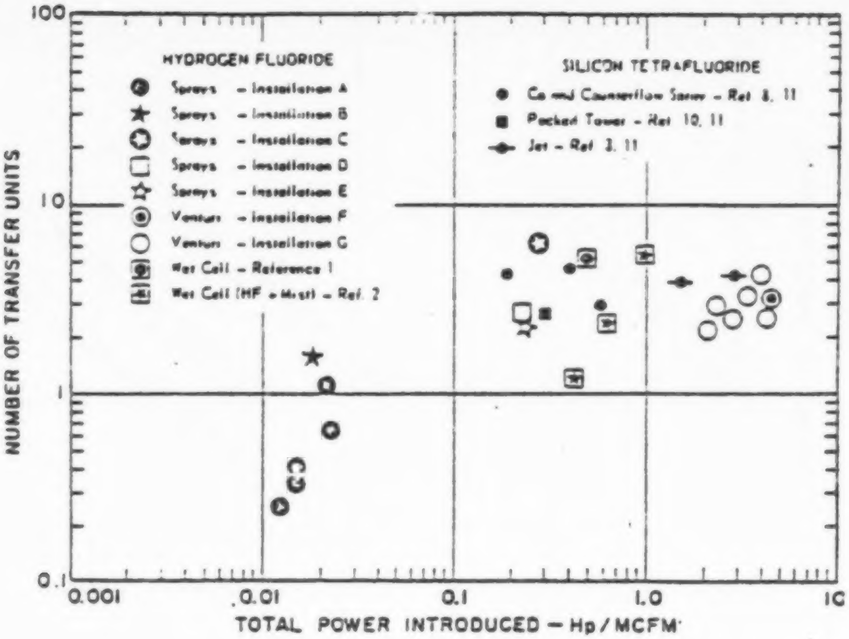

Figure 7-7: Power Consumed in SiF_4 Absorption

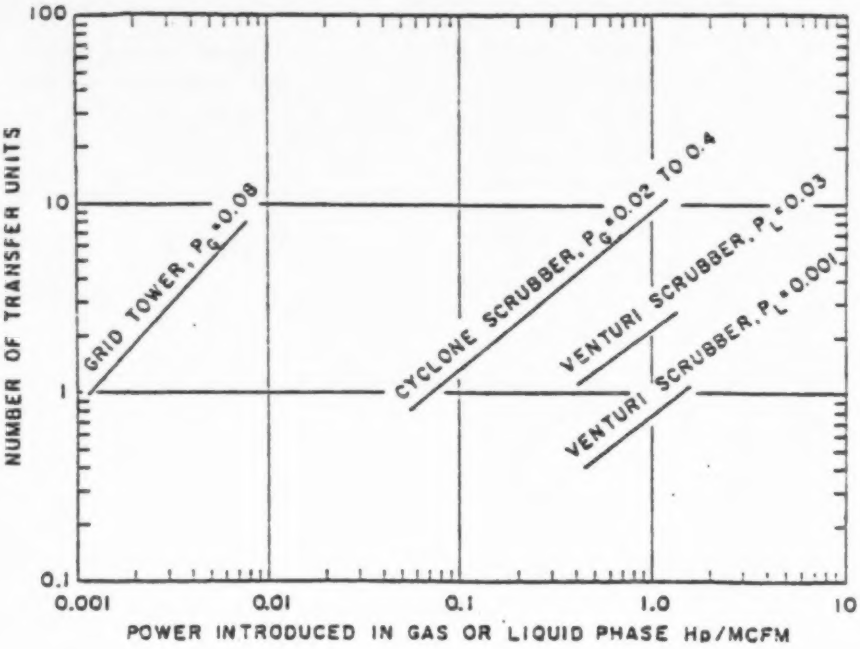

Figure 7-8: Power Consumed in Absorbing SO_2

The absorption of sulfur dioxide is analogous in many respects to the absorption of gaseous fluorides, and the relative performance of equipment should be similar. It was shown that the number of transfer units obtainable on grid towers is controlled principally by tower height and is only slightly affected by power expended on the liquid and gas phases. The performance of cyclone spray scrubbers is primarily a function of power expended in the liquid phase and is essentially independent of the power expenditure in the gas phase. Performance of Venturi scrubbers, on the other hand, depends largely on the power expended in the gas phase but is slightly affected by liquid power expenditure. These results are useful in characterizing the dominant factors in the performance of equipment used in the absorption of gaseous fluorides.

Nearly all usable data from the absorption of hydrogen fluoride are based upon application of spray towers. The performance of this equipment appears to be dominated by the power expended on the liquid phase, as was the case with the cyclone scrubber. Significant differences in performance among the various spray towers in use were found. Wet-cell washers require a higher power consumption than simple spray towers with the same performance.

The performance of spray towers absorbing silicon tetrafluoride is not consistent with simple gas absorption. One possible explanation is that mists are formed in the tower, which are collected primarily in the entrainment separators just prior to emergence from the tower. The mist is probably rather coarse, however, because high-power consuming devices such as jet scrubbers do not exhibit substantially better performance than the low-power-consuming spray towers.

In an HF manufacturing plant, the packed tower is most frequently used for emission control.

One important factor in packed tower design is the type and size of packing since it determines the efficiency, pressure drop, and flow rates at which the flooding will occur. In the air pollution control application of the packed tower, rather low concentration of gases in the air stream are usually encountered. Therefore, there is generally no need for a higher liquid flow rate than that required for complete irrigation.

The quantities which are ordinarily fixed before a packed tower is designed are:

1. Volumetric air flow rate, composition and temperature of entering gas.
2. Composition and temperature of entering liquid (but not flow rate).
3. Pressure.
4. Heat gain or loss.

Under these circumstances, it can be shown that the principal variables still remaining are:

1. The liquid flow rate (or liquid/gas ratio).
2. Height of packing (retention time).
3. The fractional absorption of any one component.

Any two of these last, but not all three, may be arbitrarily fixed by a given design. The fractional absorption of HF, SiF_4, and SO_2 depends on the liquid used in the packed tower. Three types of liquid are used in the

HF industry: acidic gypsum pond water, neutral plant water, and an alkaline liquor containing lime or caustic. The efficiency of the equipment depends on the choice of scrubbing liquid. There are no reliable data on fluoride removal efficiency but it appears that acidic liquid would have an efficiency of 60 to 90%, neutral water about 90%, and caustic up to 99%. Consequently, a packed tower with about 5 transfer units and an alkaline scrubbing liquid with a pH of about 10-11 presents the best available control technology.

7.3 Fugitive Emission Control

The major source of fugitive spar emission is usually the spar pile. Under windy conditions, spar can become airborne and drift beyond the plant property line especially when the pile is being worked. The best control for spar emission is to keep it in a storage building or silos. Less effective techniques are to cover the pile with a tarp or use dust suppressing chemicals. Fugitive emissions of spar in plant transport are best-controlled by baghouses. The conveyor lines should be kept under negative pressure to prevent emission.

The reactor kiln is under 1/2 to 1 in. wg negative pressure under normal operating conditions. Under upset conditions, the kiln can become a source of concentrated HF emissions. Most plants practice one of twc control alternatives. The first is to have a standby scrubber connected to a kiln. The scrubber is usually a packed bed with caustic as a scrubbing liquid. The gas stream is separated from the scrubber by a rupture disc which is ruptured manually in case of emergency. Some plants have a provision to short-circuit the absorption train and go directly to the final scrubber in case of emergency. The standby scrubber is a better concept and represents the best available technology. Only 2 or 3 plants have no provision to control kiln fugitive emissions. Most of the gypsum ponds used in HF manufacture are either neutralized with lime or have an excess of lime resulting in a pond pH of 10-11. A few plants have acidic ponds with a pH of 1 which can be a source of HF and SiF_4 emission. The best method for control of acidic ponds is liming. Once the pH of pond water is brought to 5-7, no fluoride emissions are expected. The second alternative is to use dry anhydrite treatment similar to the Buss Process.

Another source of HF fugitive emissions is tank car loading and unloading. Figure 7-9 shows the emission control during tank car unloading. At least one plant is known to have HF fugitive emission problems during tank car loading/unloading.

7.4 Summary of Best Control Technology

There is no one single plant that uses the best control technology on all emission sources. Some plants have better control on one source; some on another. It appears that implementation of New Source Performance Standards would result in equalizing control efforts throughout industry. Table 7-3 summarizes the best available control technology for HF manufacturing plants. Since fluoride is not a criteria pollutant NSPS would make it a designate pollutant and regulation would apply to existing facilities. If the best control technology were practiced in all plants the overall fluoride emissions would be reduced by 20-30%.

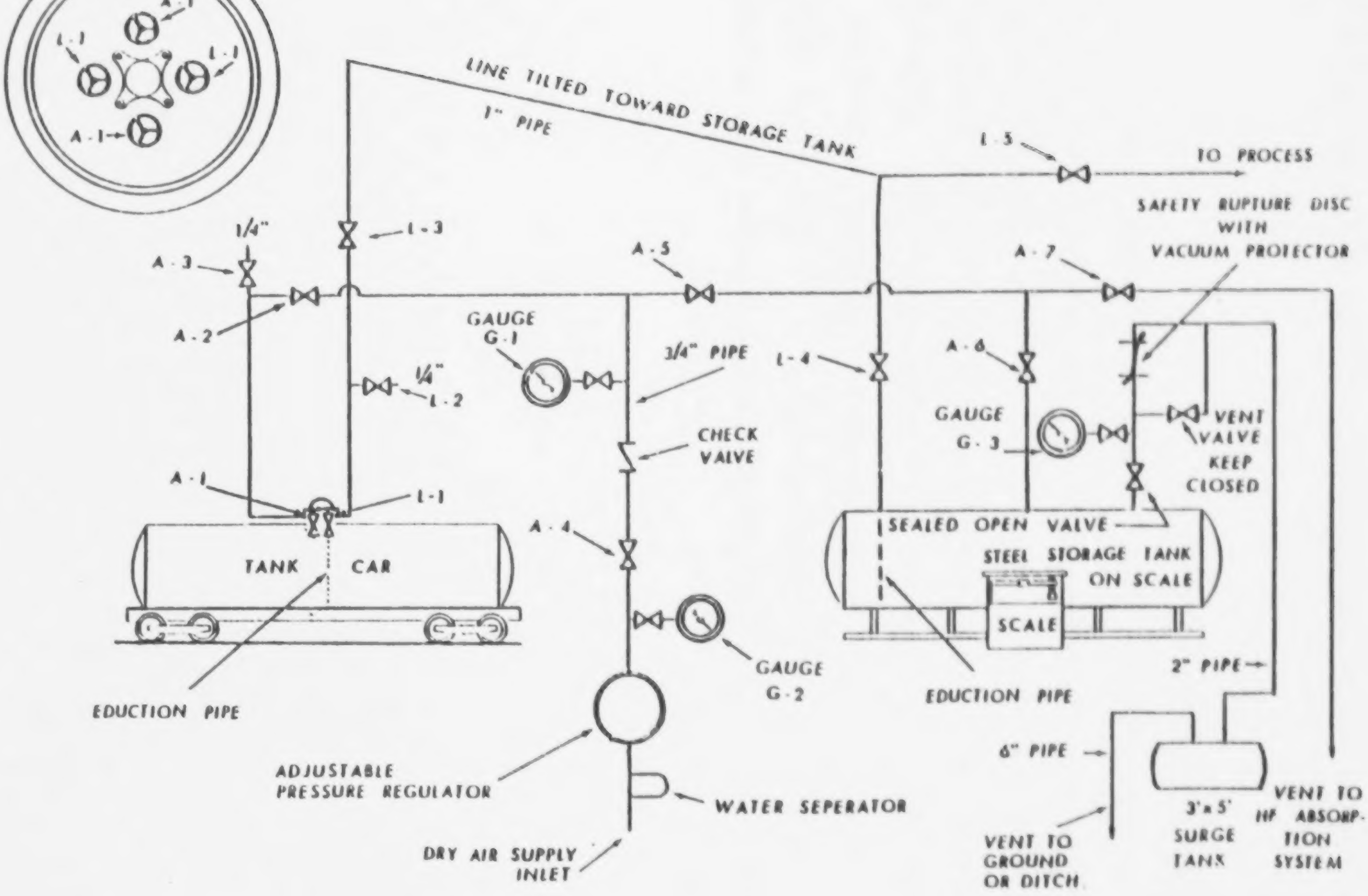
A-1
L-1
L-1
A-1
LINE TILTED TOWARD STORAGE TANK
1" PIPE
L-5
TO PROCESS
SAFETY RUPTURE DISC
WITH
VACUUM PROTECTOR
1/4"
A-3
L-3
A-2
A-5
A-7
GAUGE
G-1
3/4" PIPE
L-4
A-6
1/4"
L-2
GAUGE
G-3
VENT
VALVE
KEEP
CLOSED
CHECK
VALVE
A-1
L-1
A-4
SEALED OPEN VALVE
TANK
CAR
STEEL STORAGE TANK
ON SCALE
SCALE
GAUGE
G-2
2" PIPE
EDUCTION PIPE
EDUCTION PIPE
6" PIPE
ADJUSTABLE
PRESSURE REGULATOR
WATER SEPERATOR
DRY AIR SUPPLY
INLET
VENT TO
GROUND
OR DITCH
3'x5'
SURGE
TANK
VENT TO
HF ABSORP-
TION
SYSTEM

Figure 7-9: Typical Tank Car Unloading Connections When Using Compressed Air for Unloading Anhydrous Hydrofluoric Acid[7]

TABLE 7-3

BEST CONTROL TECHNOLOGY IN HF MANUFACTURE

Source	Pollutant	Control Equipment	Efficiency %
Spar dryer	Spar particulate	Fabric filter	99
Spar handling and storage	Spar fugitive	Storage building or silo plus fabric filter	99
Tail gas	HF, SiF_4, SO_2	Caustic scrubber	99
Kiln upset	HF, SiF_4, SO_2	Caustic scrubber	90
Gypsum pond if acidic	HF, SiF_4	Liming	99+
HF loading/ unloading	HF	MCA* Procedure	99+
HF dilution	HF	Caustic scrubber	99

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*MCA - Manufacturing Chemists Association

7.5 References

1. Billings, C.E., Fabric Filter Manual, The McIlvaine Co., Northbrook, Illinois, 1975.

2. Strauss, W., Industrial Gas Cleaning, p. 214, Pergamon Press, 1966

3. The McIlvaine Scrubber Manual, The McIlvaine Co., 1974.

4. Air Pollution Engineering Manual, Danielson, J.A., Ed., EPA, OAQPS, May 1973.

5. Boscak, V., Tendon, J., Odor Abatement in Animal Food Manufacturing Plants, Proceedings of the First Conference on Energy and Environment, College Corner, Ohio, 1973.

6. Lunde, K.E., Performance of Equipment for Control of Fluoride Emissions, p. 293-298, Ind. Eng. Chem., Vol. 50, No. 3, March 1958.

7. Hydrofluoric Acid, Chemical Safety Data Sheet SD-25, Manufacturing Chemists Association, Washington, DC, 1970 (Rev.).

8.0 STATE AND LOCAL EMISSION REGULATIONS

The following sections discuss the state and local regulations applicable to HF manufacturing and summarize these regulations. The values in this section are given in the units that appear in the regulations.

8.1 Summary Of Applicable Emission Regulations

Although hydrofluoric acid manufacturing is regulated under the permit and particulate regulations of the states where operations exist, no states have adopted regulations which specifically address HF production. Rather, states treat HF manufacturing as a process industry for purposes of air pollution control regulations. As such, eight types of control requirements apply depending upon the particular jurisdiction:

1. General process weight limitations, typically using the following equation:

   $E = 4.10\ (P)^{0.67}$ where $P < 30$ tons/hr

   $E = [55.0\ (P)^{0.11}] - 40$ where $P \geq 30$ tons/hr

   Where

   E represents allowable emission rate (lb/hr) and P represents process weight rate (tons/hr)

2. Mass particulate emissions limitations. These are generally expressed in terms of allowable grains or pounds of particulate per standard cubic foot.
3. Control efficiency limitations. The States of Ohio and New Jersey use this approach.
4. Control based upon the stack gas flow rate. Texas uses this type of regulation.
5. Visible emissions limitations. These are applicable in virtually all states studied.

6. Fugitive emissions limitations. These apply in most states studied.
7. Ambient and emissions limitations for fluorides. These apply in three of the states covered by this study: Kentucky, Louisiana, and Texas.
8. "Catch-all" provisions. A number of states have such provisions which are intended to control toxic or hazardous emissions on a case-by-case basis.

The conclusion drawn from this analysis of State regulations is that process weight and/or fluoride emissions standards apply to HF manufacturing in virtually all states where operations exist. The level of enforcement of these regulations is moderate and no State agency indicated that emissions from this industry was a top agency priority.

8.2 List of Regulations Applicable to the Hydrofluoric Acid Manufacturing Industry

Tables 8-1 through 8-9 present the State and local regulations on particulate emissions, process weights, visible emissions, fugitive emissions, fluoride standards, and other related areas. Table 8-10 summaries the state regulations on allowable fluoride emission.

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TABLE 8.1. San Francisco Bay Area Regulations Applicable to HF Manufacturing[1]

Plants	Particulate Matter Emission Limits	Process Weight Equation (See Key for Explanation)	Visible Emissions	Fugitive Emissions	Fluoride Standards Ambient	Fluoride Standards Emissions	Other Applicable Regulations
The Allied Facility at Pittsburg is under the jurisdiction of the Bay Area Air Pollution Control District.	Regulation 2 of the Bay Area District establishes both a maximum grain loading for industrial process operations of 0.15 gr/scfm and a process weight limitation. In addition, the Bay area has a total mass emission ceiling of 40 lb/hour regardless of the type or size of the source.	A	Regulation 2 establishes a visible emission limit of No. 1 on the Ringlemann Chart (20% capacity). This level may not be exceeded for more than 3 minutes per hour.	Not applicable	Not applicable	Not applicable	None

PROCESS WEIGHT EQUATIONS

Key:

(A) $E = 4.10\ (P)^{0.67}$ (Regardless of P Value)

(B) $E = 4.10\ (P)^{0.67}$ ($P <$ tons/hr)

$E = 155.0\ (P)^{0.11}1 - 40.0$ ($P \geq 30$ tons/hr)

Where:

E = Allowable emission rate in pounds per hour, and

P = Process weight rate in tons per hour

TABLE B 2. Kentucky State Regulations Applicable to HF Manufacture[2]

Plants	Particulate Matter Emission Limits	Process Weight Equation (See Key for Explanation)	Visible Emissions	Fugitive Emissions	Fluoride Standards Ambient	Fluoride Standards Emissions	Other Applicable Regulations
The Pennwalt facility at Calvert City, Kentucky is subject to the State Air Pollution Control requirements of the Kentucky Division of Air Pollution Control	401 Kentucky Administrative Regulations, Section 3:050(4), establishes Standards of Performance for process operations. This regulation allows owners to comply with either a process weight limitation or a mass particulate emission limitation of 0.02 grains per standard cubic foot at a minimum of 97% actual removal efficiency	B	In addition to the process weight and mass particulate emissions limitations of 401 KAR 3:060(4), visible particulate emissions are limited to 40% capacity.	Kentucky's fugitive emission regulation 401 KAR 3:060(14), requires (and enumerates) all reasonable precautions and prohibits the discharge of visible fugitive dust emissions beyond the property line.	401 KAR 3:020 (8)-Primary Standard for Gaseous Fluoride(as HF) Time-avg. (not to be exceeded more than once/yr.) — Standard ($\mu g/m^3$) 1 month — 0.82 1 week — 1.64 24-hour — 2.68 12-hour — 3.68 401 KAR 3:020(9)-Primary Standards for Total Fluorides (as fluoride ion) (a) Not to exceed 40 ppm (w/w) average concentration of monthly samples over growing season (not to exceed 6 consecutive months). (b) Not to exceed 60 ppm (w/w)-2-month average. (c) Not to exceed 80 ppm (w/w)-1-month average.	Not Applicable	Section 3 of 401 KAR 3:040 provides for a case-by-case evaluation of potentially hazardous emissions. This regulation is applicable to several of the more harmful emissions from hydrofluoric acid plants, including acid mist.

PROCESS WEIGHT EQUATIONS

Key:

(A) $E = 4.10 (P)^{0.67}$ (Regardless of P Value)

(B) $E = 4.10 (P)^{0.67}$ ($P <$ tons/hr)

$E = 155.0 (P)^{0.11} - 40.0$ ($P \geq 30$ tons/hr)

Where:

E = Allowable emission rate in pounds per hour, and

P = Process weight rate in tons per hour

TABLE 8-3. Louisiana State Regulations Applicable to HF Manufacturing[3]

Plants	Particulate Matter Emission Limits	Process Weight Equation (See Key for Explanation)	Visible Emissions	Fugitive Emissions	Fluoride Standards		Other Applicable Regulations
					Ambient	Emissions	
The Allied facilities at Baton Rouge and Geismar and the Kaiser plant at Gramercy are all governed by the Louisiana State Air Pollution Control Regulations.	Section 19.5 of the Louisiana Air Pollution Control Regulations establishes a general process weight standard. Under Section 19.8, the State may tighten these limits for toxic particulate emissions.	B	Section 19.5.1 establishes a general 20% opacity standard which may be exceeded for not more than 4 minutes in any consecutive 60 minutes.	Section 19.1 specifies that all reasonable precautions must be taken to prevent particulates from becoming airborne. Seven such precautions are specified, including the use of dust collectors.	Although Louisiana does not have an ambient fluoride standard, Section 8.2 of the regulations prohibits emissions which will cause "undesirable levels" (i.e., harmful to humans, animals plants or property) of any air pollutant. This has direct application to fluorides and acid mists emitted by hydrofluoric acid plants.	Although there are no specific fluoride emission standards applicable to HF manufacturing in Louisiana, sections 8.2, 9.2.1, and 17.10 prohibit emissions which would cause "undesirable levels" of any pollutant. The Louisiana Air Control Commission has administratively implemented this authority by establishing a 24-hr equivalent ambient fluoride standard of 1/20 T.L.V. at the property line.	Under Sections 9.2.1 and 19.8.1, the Louisiana Air Quality Section has the authority to establish particulate emission standards for potentially toxic pollutants which are more stringent than would otherwise apply.

PROCESS WEIGHT EQUATIONS

Key:

(A) $E = 4.10 (P)^{0.67}$ (Regardless of P Value)

(B) $E = 4.10 (P)^{0.67}$ (P < tons/hr)

$E = 155.0 (P)^{0.11} - 40.0$ (P ≥ 30 tons/hr)

Where:

E = Allowable emission rate in pounds per hour, and

P = Process weight rate in tons per hour

TABLE 8-5. Ohio State Regulation Applicable to HF Manufacturing[4]

Plants	Particulate Matter Emission Limits	Process Weight Equation (See Key for Explanation)	Visible Emissions	Fugitive Emissions	Fluoride Standards		Other Applicable Regulations
					Ambient	Emissions	
The Harshaw facility in Cleveland is subject to State Regulations as well as local regulations of the City of Cleveland. The State requirements are presented in this table.	Regulation 3745-17-11 of the Ohio Air Pollution Control Regulations limits all industrial emissions to the more stringent of two levels: (1) a process weight limit (see next column) or (2) a percent efficiency reproduced in Fig. 8-1. Figure 8-1 relates Uncontrolled Mass Rate of Emission (abscissa) to maximum allowable mass rate of emission (ordinate). The process weight limit relates process weight of materials introduced into an specific process that may cause any emission of particulate matter to maximum allowable mass rate of emission. The process weight limit shall apply in nonattainment areas for TSP where the Uncontrolled Mass Rate of Emission cannot be ascertained and where an emission factor characterization for the process is unknown. Curve P-1 of	B	State Regulation 3745-17-07 establishes a General 20% opacity limit (No. 1 Ringlemann) for all sources. A 3-minute-per hour aggregate allowance of up to 60% (No. 3 Ringlemann) is provided for.	State Regulation 3745-17-08 requires and enumerates the "reasonable precautions" required to prevent particulate matter from becoming airborne.	Not applicable	Not applicable	Section 3745-15-07 of the State Regulations is a general provision which prohibits air pollution which would unreasonably harm public health or welfare or constitute a public nuisance.

PROCESS WEIGHT EQUATIONS

Key:

(A) $E = 4.10 (P)^{0.67}$ (Regardless of P Value)

(B) $E = 4.10 (P)^{0.67}$ (P < tons/hr)

$E = 155.0 (P)^{0.11} - 40.0$ (P ≥ 30 tons/hr)

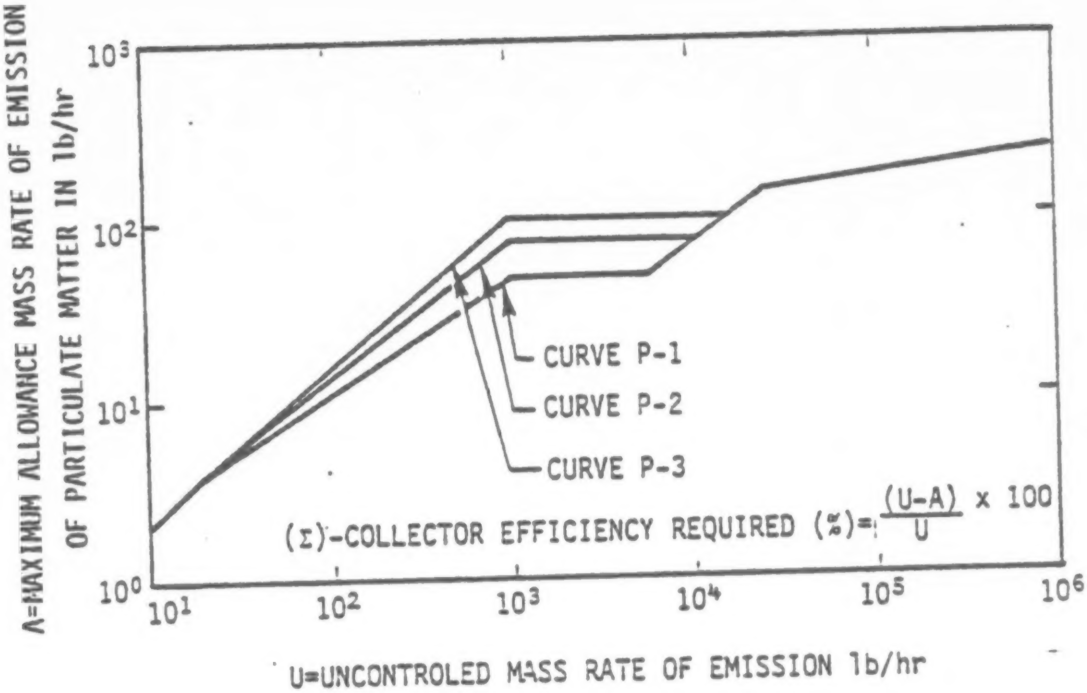
Where:

E = Allowable emission rate in pounds per hour, and

P = Process weight rate in tons per hour

TABLE 8-4 (cont.) Ohio State Regulations Applicable to HF Manufacturing[4]

Plants	Particulate Matter Emission Limits	Process Weight Equation (See Key for Explanation)	Visible Emissions	Fugitive Emissions	Fluoride Standards		Other Applicable Regulations
					Ambient	Emissions	
	Figure 8-1 shall apply in Priority I regions where the Process Weight Rate cannot be ascertained. In all cases, the more stringent of the two requirements shall apply where both are termed applicable.						



NOTE: AFTER JULY 1, 1975, CURVE P-1 APPLIES IN ALL CASES WHERE THIS REQUIREMENT IS DEEMED APPLICABLE.

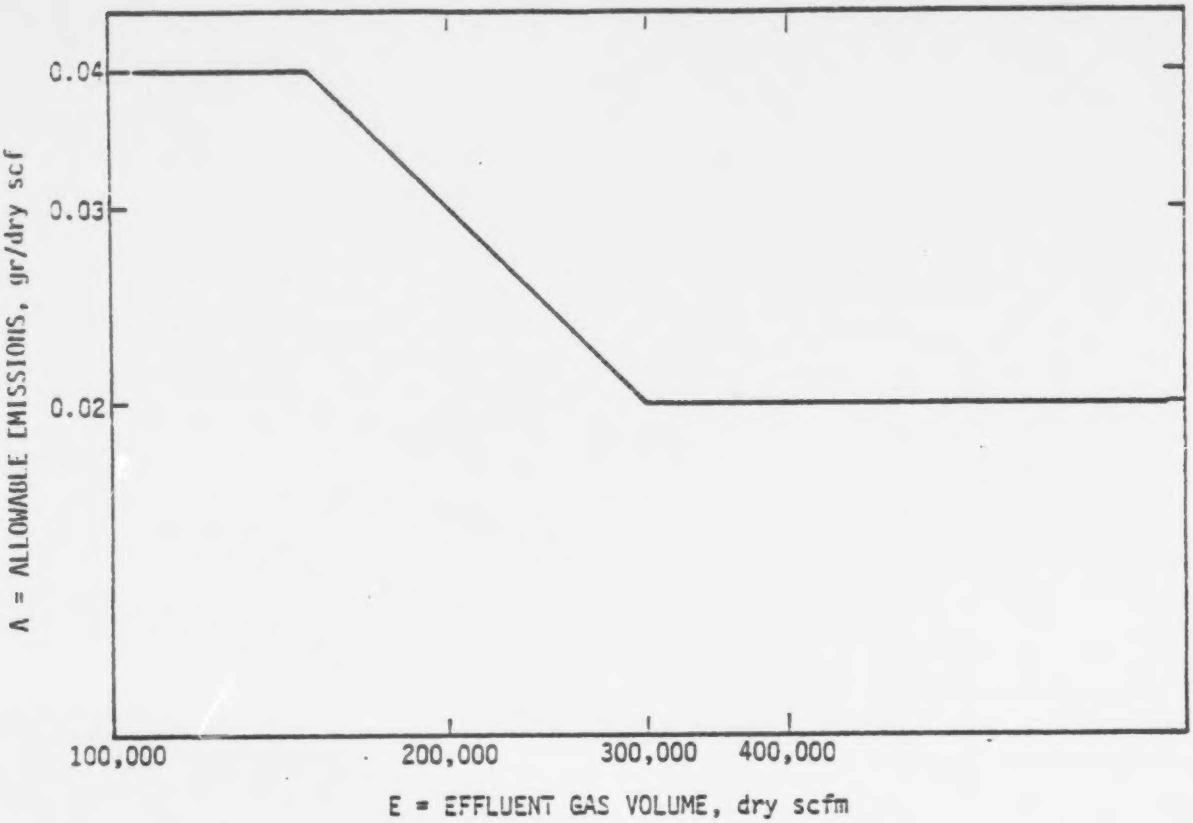
Figure 8-1: Ohio Collector Efficiency Curve[4]

TABLE 8-5. City of Cleveland Regulations Applicable to HF Manufacturing[5]

Plant	Particulate Matter Emission Limits	Process Weight Equation (See Key for Explanation)	Visible Emissions	Fugitive Emissions	Fluoride Standards		Other Applicable Regulations
					Ambient	Emissions	
The Harshaw facility in Cleveland is subject to State Regulations, as well as local regulations of the City of Cleveland. The State requirements are presented in Table 8-4.	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Section 277.06 of the Cleveland Air Pollution Control Regulations regulates gaseous HF emissions from hydrofluoric acid manufacturing, blending, storage and loading operations, as follows: MANUFACTURING - 0.4 lbs of HF/ton of anhydrous HF acid produced from anhydrous gas production operations per hour. BLENDING - 0.15 lbs of HF/ton of 70% HF acid produced per hour. STORAGE AND LOADING - 0.45 lbs of HF/ton of anhydrous HF acid stored or loaded per hour.	Not Applicable

TABLE 8-6. Pennsylvania Commonwealth Regulations Applicable to HF Manufacturing[6]

Plants	Particulate Matter Emission Limits	Process Weight Equation (See Key for Explanation)	Visible Emissions	Fugitive Emissions	Fluoride Standards		Other Applicable Regulations
					Ambient	Emissions	
Neither the Ashland facility at Glendon nor the Allied plant at Marcus Hook are currently manufacturing HF. Nevertheless, the regulations which would be applicable to such operations are included for informational purposes.	Section 123.13 of the Pennsylvania Air Resources Regulations regulates particulate matter emissions from process operations. For process operations not specifically listed (HF Manufacturing is an unlisted process) allowable emissions are graphically illustrated in Figure 8-2.	Not Applicable	Section 124.41 prohibits visible emissions, the opacity of which: 1) equals or exceeds 20% for an aggregate or more than 3 minutes in any one hour, or 2) equals or exceeds 60% at any time. This limitation does not apply to fugitive emissions which are permitted under section 123.1 (see next column).	Section 123.1(a)(9) prohibits fugitive emissions unless the Pennsylvania DER determines such emissions are of minor significance and are not preventing the attainment or maintenance of any ambient standard. Sec. 123.1(c) specifies certain reasonable precautions to prevent fugitive emissions-Sec. 123.2 prohibits fugitive particulate emissions at the property line which are either visible or exceed 150 particles/cubic/cm.	Chapter 131 of the Pennsylvania Regulations establishes a 24-hour fluoride standard of 5 $\mu g/m^3$ (total soluble as HF).	Under Section 127.22, operating permit applications must upon request show that the source will not violate any ambient air quality standard.	Section 121.7 sets forth a general prohibition against "air pollution."



THIS GRAPH TRANSLATES AS FOLLOWS:

(i) 0.04 GRAINS PER DRY STANDARD CUBIC FOOT, WHEN THE EFFLUENT GAS VOLUME IS LESS THAN 150,000 DRY STANDARD CUBIC FEET PER MINUTE.
(ii) THE RATE DETERMINED BY THE FORMULA:
$A = 6000E^{-1}$, WHERE:

A = ALLOWABLE EMISSIONS IN GRAINS PER DRY STANDARD CUBIC FOOT, AND
E = EFFLUENT GAS VOLUME IN DRY STANDARD PER CUBIC FEET PER MINUTE,
WHEN E IS EQUAL TO OR GREATER THAN 150,000 BUT LESS THAN 300,000.
(iii) 0.02 GRAINS PER DRY STANDARD CUBIC FOOT, WHEN THE EFFLUENT GAS VOLUME IS GREATER THAN 300,000 DRY STANDARD CUBIC FEET PER MINUTE.

Figure 8-2: Pennsylvania Allowable Emissions Curve for Sources Not Listed in Section 123.13[6]

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TABLE 8-7. Texas State Regulations Applicable to HF Manufacturing[7]

Plants	Particulate Matter Emission Limits	Process Weight Equation (See Key for Explanation)	Visible Emissions	Fugitive Emissions	Fluoride Standards		Other Applicable Regulations
					Ambient	Emissions	
The Alcoa, Dupont and Stauffer plants in Point Comfort, La Porte and Greens Bayou respectively are all subject to Texas State Air Pollution Control Regulations.	Rule 105 of Texas Regulation I establishes particulate matter emissions limitations for sources other than those processing or handling agricultural commodities. Sources subject to Rule 105 must conform to the allowable emission rates as shown in Figure 8-3 and/or Figure 8-4. Each regulates emissions according to the effluent flow rate of the source adjusted for stack height. In addition, Rule 105 establishes an ambient air quality-related emission standard which prohibits particulate emission which would cause any of the time-averaged net ground level particulate concentrations to be exceeded:	Not Applicable	Rule 103 of Texas Regulations I prohibits excessive visible emissions from any enclosed building or facility. With respect to stack emissions, the rule specifies a 30% opacity limit, averaged over a 5-minute period. Stacks constructed after January 31, 1972, are limited to 20% opacity on a 5-minute average.	Rule 104 of Texas Regulation I establishes and enumerates "reasonable precautions" which must be adopted to prevent particulates from becoming airborne in areas which are nonattainment for the ambient particulate standard.	See Figure 8-5.	See Figure 8-5.	Rule 5 is a general nuisance statute applicable to air pollution.

TABLE H-7. (cont.) Texas State Regulations Applicable to HF Manufacturing[f]

Plants	Particulate Matter Emission Limits		Process Weight Equation (See Key for Explanation)	Visible Emissions	Fugitive Emissions	Fluoride Standards		Other Applicable Regulations
						Ambient	Emissions	
	Time Avg. (hrs)	Concentration ($\mu g/m^3$)						
	5	100						
	3	200						
	1	400						

Effluent Flow Rate acfm	Rate of Emission lb/hr
1,000	3.5
2,000	5.3
4,000	8.2
6,000	10.6
8,000	12.6
10,000	14.5
20,000	22.3
40,000	34.2
60,000	44.0
80,000	52.6
100,000	60.4
200,000	92.9
400,000	143.0
600,000	184.0
800,000	219.4
1,000,000	252.0

Interpolation and extrapolation of the data in this table shall be accomplished by the use of the equation $E = 0.048\ q^{0.62}$ where E is the allowable emission rate in lb/hr and q is the stack effluent flow rate in acfm.

Figure 8-3: Texas Allowable Particulate Emission Rates for Specific Flow Rates[7]

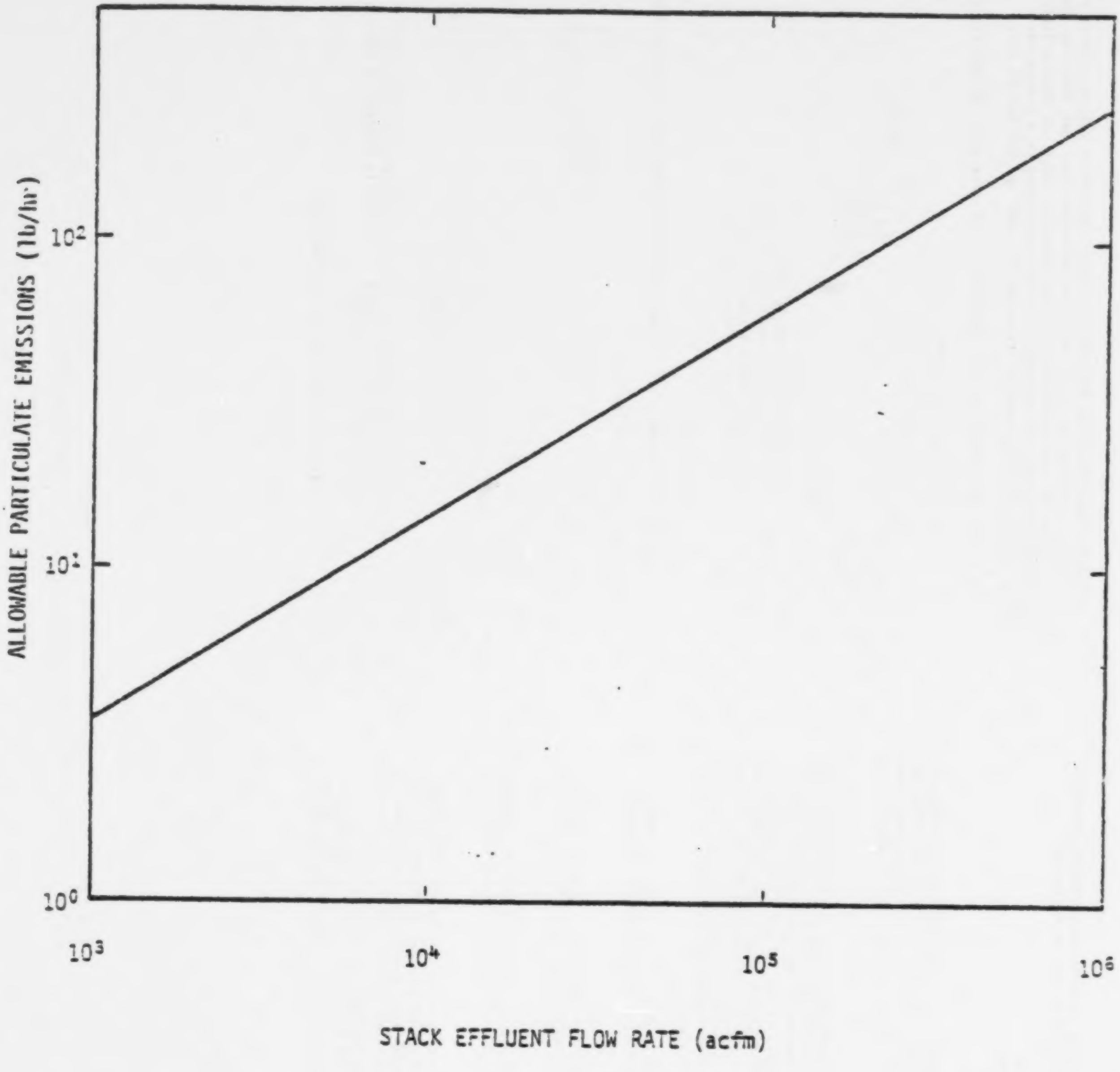


Figure 8-4: Texas Allowable Particulate Emission Rates for Specific Flow Rates[7]

a. The Board declares that concentrations of gaseous inorganic fluoride compounds in the atmosphere, calculated as HF, in excess of:

4.5 ppb for any 12-hour period
3.5 ppb for any 24-hour period
2.0 ppb for any 7-day period
1.0 ppb for any 30-day period

by volume at 760 mm Hg and 25 degrees C average constitute undesirable levels, whether the sources are from natural causes or from the activities of man, and that a state of air pollution exists when concentrations of any gaseous inorganic fluoride compound, calculated as HF, exceed any of these levels.

b. The Board further declares that concentrations of inorganic fluoride compounds in forage located in a Type D land use area, including inorganic fluoride compounds both absorbed in and deposited on forage, calculated as fluoride ion, in excess of any of the following levels indicate the presence of undesirable levels in the area in which the forage is grown, whether the sources are from natural causes or from the activities of man; and that a state of air pollution exists when concentrations of inorganic fluoride compounds, calculated as fluoride ion, exceed any of the specified levels:

(1) An average of 40 parts per million by weight based on samples taken once a month over a period of 12 consecutive calendar months; or

(2) An average of 60 parts per million by weight based on samples taken once a month over a period of three consecutive calendar months; or

(3) An average of 80 parts per million by weight based on samples taken once a month over a period of two consecutive calendar months.

To assist in meeting the ambient air quality standards, the Board hereby establishes a limit on the emission of gaseous inorganic fluoride compounds, calculated as HF, which may be made from any property not to exceed 6 parts per billion by volume average during a period of 3 consecutive hours. The contribution of inorganic fluoride compounds by a single property shall be measured by the difference between the upwind level and the downwind level of inorganic fluoride compounds for the property, or by stack sampling calculated to a downwind concentration.

The maximum allowable fluoride emission rate which may be made from a stack on a property to comply with the emission limit set forth in this Regulation may be calculated by Sutton's Equation which has been modified to consider the critical wind speed and to correspond to a 3-hour air sample. The equations used for fluoride for cold and hot stacks are:

1. For exit stack gas for temperatures of less than 125 degrees F.

(a) All land use types

$$Qa = 5.8 \times 10^{-5} V_s d_s^2 \qquad \frac{1}{\left[\frac{d_s}{h_s}\right]^{1.29}}$$

Where:

Qa = emission rate lbs/hr.
V_s = stack exit velocity, ft/sec.
d_s = exit stack diameter, ft.
h_s = physical stack height, ft.

(See Graph 1.)

2. For exit stack gas for temperatures greater than 125 degrees F.

(a) All land types

$$Qa = 1.28 \times 10^{-4} V_s d_s \quad \left[1.5 + 0.82 \left(\frac{\Delta T}{T_s}\right) d_s \qquad h_s\right]$$

Where:

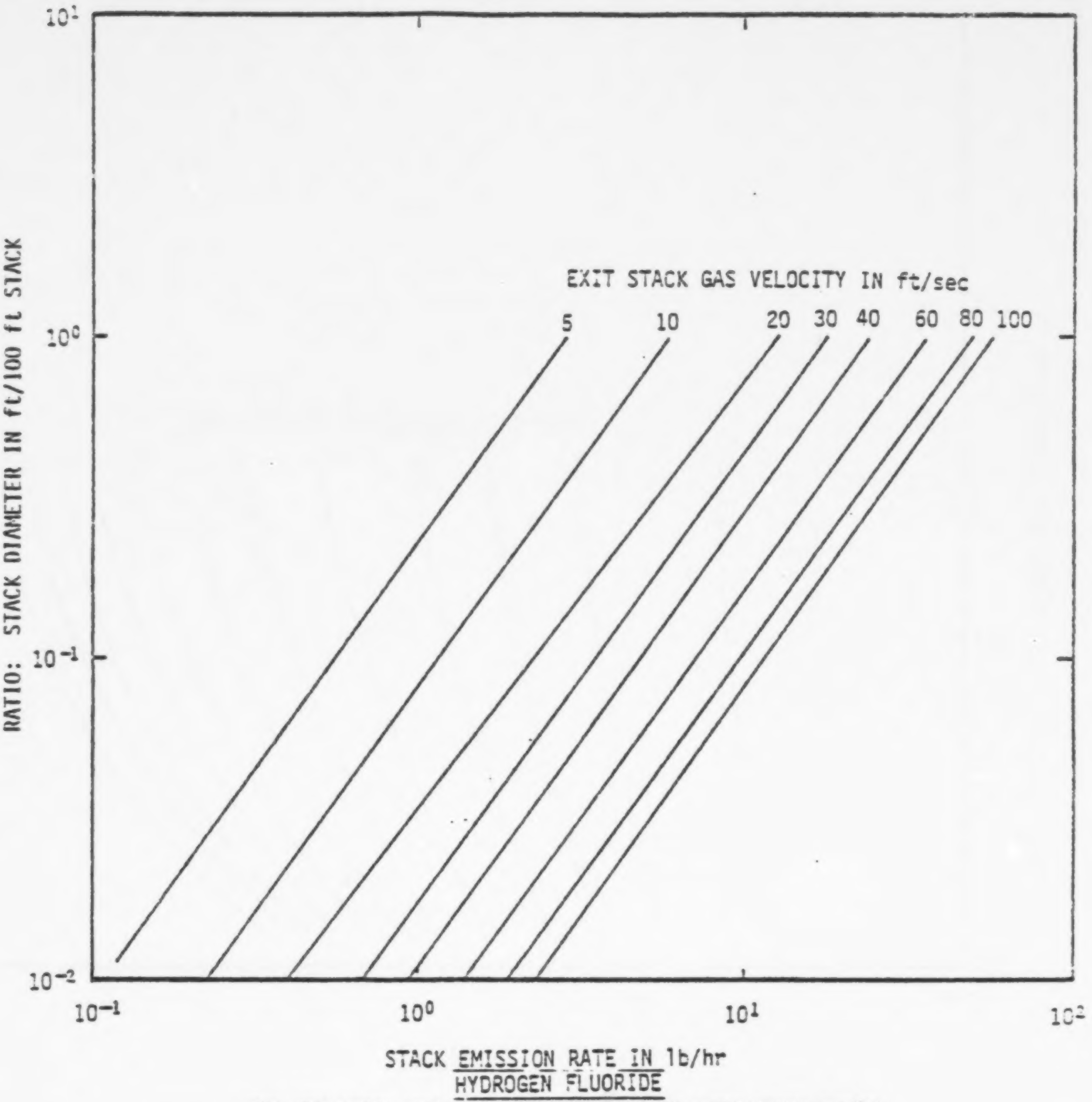
Qa = emission rate, lbs/hr.
V_s = stack exit velocity, ft/sec.
d_s = exit stack diameter, ft.
h_s = physical stack height, ft.

ΔT = temperature difference between stack gas and the outdoor temperatures of 90°F. (550°R) is assumed in preparing dispersion graphs.

T_s = stack exit temperature in °Rankine.

(See Graph 2.)

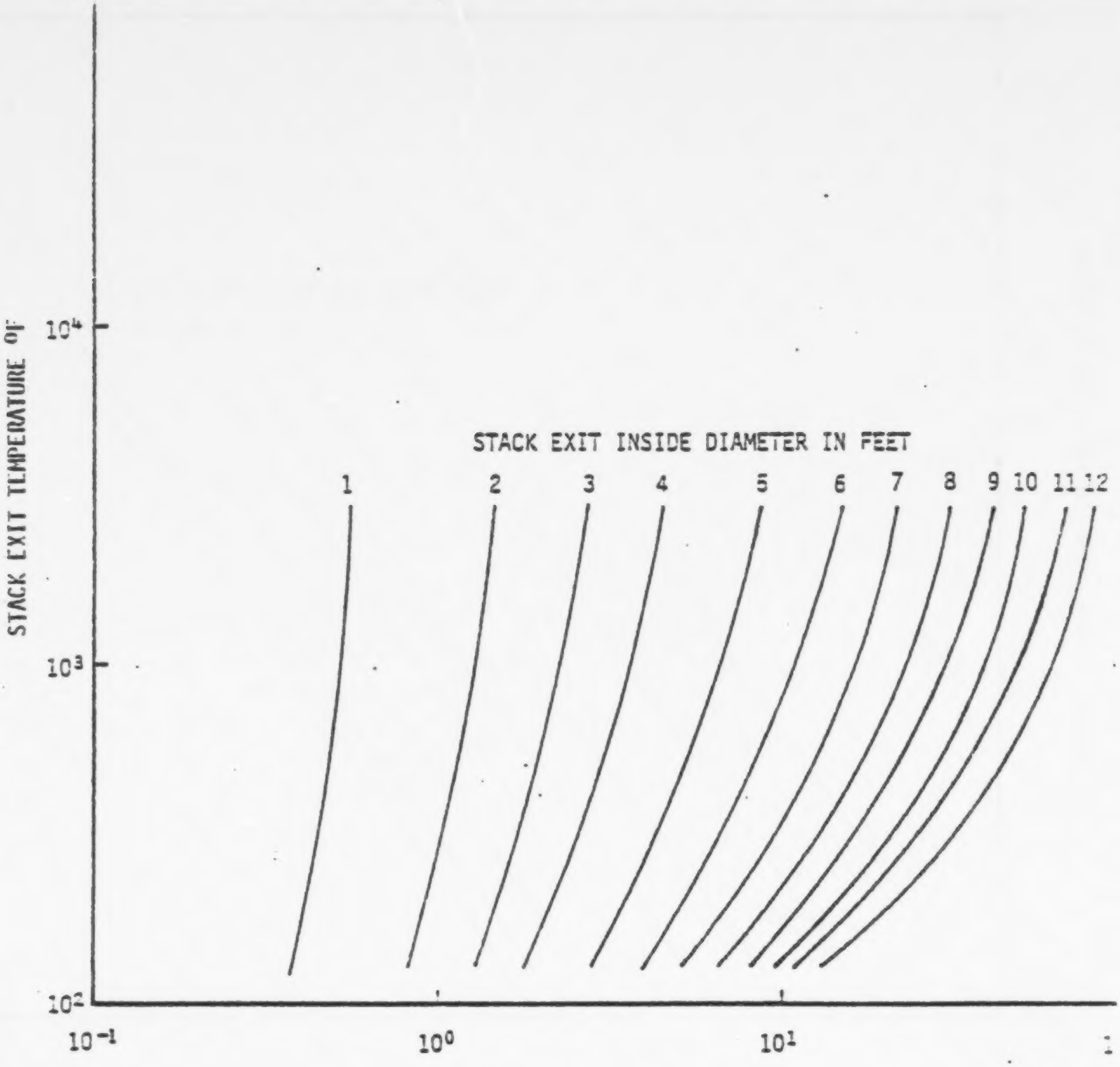
Figure 8-5: Texas Fluoride Standards
(Key Excerpts from Regulation III)[7]



FOR USE WHEN THE EXIT TEMPERATURE IS LESS THAN 125°F

TO PLOT GRAPH 1, ASSUME A BASIC STACK HEIGHT OF 100 FEET AND PLOTS $\frac{d_s}{100}$ 1.29 FOR VARIOUS STACK DIAMETERS VERSUS STACK VELOCITY.

Figure 8-5: (continued) Graph 1



STACK EMISSION RATE IN lb/hr
HYDROGEN FLUORIDE
FOR USE WHEN THE EXIT TEMPERATURE IS GREATER THAN 125°F

TO PLOT GRAPH 2, ASSUME A BASIC STACK HEIGHT OF 100 FEET AND AN EXIT VELOCITY OF 20 ft/sec. LET STACK GAS

Figure 8-5: (continued) Graph 2

TABLE B-8. West Virginia State Regulations Applicable to HF Manufacturing[a]

Plants	Particulate Matter Emission Limits	Process Weight Equation (See Key for Explanation)	Visible Emissions	Fugitive Emissions	Fluoride Standards		Other Applicable Regulations
					Ambient	Emissions	
The Allied facility at Nitro, W. Va. is subject only to state air pollution regulations.	Regulation III of the West Virginia Air Pollution Regulations governs particulate emissions from manufacturing process operations. HF acid manufacturing is a type "d" source under Regulation VII and would theoretically be subject to the process weight limitations applicable to such sources. However, mineral acid emission are not covered by the State's process weight regulation. Furthermore, the section on mineral acid emissions doesn't apply to HF. Therefore, HF particulate emissions from HF plants are governed by Sections 2, 3.13 and 4 of Regulation VII.	Not Applicable	Section 2 of Regulation VII prohibits smoke emissions in excess of No. 1 on Ringlemann Chart. An allowance for up to No. 2 is provided for periods aggregating no more than 5 minutes in any 1-hr. period.	Section 4 of Regulation VII requires the installation and use of fugitive particulate control systems together with suitable road paving and good operating practice standards to control fugitive dust.	Not Applicable	Not Applicable	Section 3.13 of Regulation VII regulates potentially toxic emissions.

Table 8-9. New Jersey State Regulations Applicable to HF Manufacturing[9]

Plants	Particulate Matter Emission Limits	Process Weight Equation (See Key for Explanation)	Visible Emissions	Fugitive Emissions	Fluoride Standards		Other Applicable Regulations
					Ambient	Emissions	
Essex Chem. Corp. in Paulsboro is subject to State of New Jersey Department of Environmental Protection Regulations.	Subchapter 6 of Chapter 27 of the New Jersey Administration Code establishes controls on the emission of particulates from manufacturing processes. Section 7:27-6.2 of Subchapter 6 is an emission rate/control efficiency regulation expressed in table form.	Not Applicable	Section 7:27-6.2(d) establishes a general 20% opacity limit for all sources.	None At Present	Not Applicable	Not Applicable	None

TABLE 8-10

SUMMARY OF STATE REGULATION ON ALLOWABLE FLUORIDE EMISSIONS

<table>
<tr><th>STATE</th><th>COMPANY</th><th>LOCATION</th><th>ALLOWABLE EMISSION RATE</th><th>STANDARDS</th></tr>
<tr><td>California (Bay Area)</td><td>Allied</td><td>Pittsburg</td><td>4.10 $(P)^{0.67}$</td><td>No</td></tr>
<tr><td>Kentucky</td><td>Penwalt</td><td>Calvert City</td><td>$4.10(P)^{0.67}$ $P < 30$ tons/hr
$155(P)^{0.11}-40$ $P \geq 30$ tons/hr</td><td>Yes</td></tr>
<tr><td>Louisiana</td><td>Allied/ Kaiser</td><td>Baton Rouge/ Geismar/Gramercy</td><td>Same as Above</td><td>No</td></tr>
<tr><td>New Jersey</td><td>Essex</td><td>Paulsboro</td><td>
<table>
<tr><th>Potential emission rate from source operation (lbs. per hr.)</th><th>Allowable emission rate (lbs. per hr.) (Based on 99% efficiency of collection)</th><th>Source gas emitted from source (Standard cu. ft. per min.)</th><th>Allowable emission rate (lbs. per hr.) (Based on 0.02 grains per SCF)</th></tr>
<tr><td>50 or less</td><td>00.5</td><td>3,000 or less</td><td>0.5</td></tr>
<tr><td>100</td><td>01.0</td><td>6,000</td><td>1.0</td></tr>
<tr><td>1000</td><td>10.0</td><td>35,000</td><td>6.0</td></tr>
<tr><td>2000</td><td>20.0</td><td>70,000</td><td>12.0</td></tr>
<tr><td>3000 or greater</td><td>30.0</td><td>140,000</td><td>24.0</td></tr>
<tr><td></td><td></td><td>175,000 or greater</td><td>30.0</td></tr>
</table>
</td><td>No</td></tr>
<tr><td>Ohio</td><td>Harshaw</td><td>Cleveland</td><td>$4.10(P)^{0.67}$ $P < 30$ tons/hr
$155(P)^{0.11}-40$ $P \geq 30$ tons/hr</td><td>Yes*</td></tr>
<tr><td>Pennsylvania</td><td>Allied</td><td>Marcus Hook</td><td>0.02 to 0.04 grams per dry SCF depending upon the effluent gas valume</td><td>Yes</td></tr>
<tr><td>Texas</td><td>Alcoa/ Dupont/ Stauffer</td><td>Point Comfort/ La Porte/ Green Bayou</td><td>E = 0.048 q 0.62 where "E" is the allowable emission rate in lbs/hr and "q" is the stack effluent flow rate in ACFM</td><td>Yes**</td></tr>
<tr><td>West Virginia</td><td>Allied</td><td>Nitro</td><td>No applicable process wt. limitations</td><td>No</td></tr>
</table>

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*The City of Cleveland has regulations for HF operations phrased in terms of pounds of HF per tone of product manufactured, blended or stored. For manufacturing the limit is 0.4 lbs HF/ton of anhydrous HF produced. The limits for blending and storage are 0.15 and 0.45 lbs HF/ton HF blended or stored, respectively.

**See Tables 8-3 through 8-5.

8.3 Definition of Plant Modification

The Clean Air Act defines a "modification" as

> "......any physical change in, or change in the method of operation of, a stationary source which increases the amount of any air pollutant emitted by such source or which results in the emission of any air pollutant not previously emitted. (§100 (a) (4)).

EPA NSPS regulations (40 CFR 60) implement the modification concept by narrowing its applicability to specific facilities within an entire source. As such, the regulations define a modification as any physical or operational change to an existing facility which results in an increase in the emission rate of any pollutant covered by a new source performance standard.

Typical examples of a modification within an HF plant would be:

1. Use of different packing in the scrubber.
2. Change in liquid to gas ratio in the scrubber.
3. Higher H_2SO_4 to spar ratio.

The determination of whether a physical or operational change will increase the emission rate is based, wherever possible, on AP-42 emission factors. However, where AP-42 factors do not yield a clear-cut answer, material balances, continuous monitoring data or manual emission tests must be employed. In cases where emission rate changes are difficult to determine or where industry-specific guidance is necessary the Administrator has the authority to promulgate industry-specific definitions of what constitutes a modification for any particular facility in that industry. Regardless of the definition or method employed, however, compliance with all applicable performance standards must be achieved within 180 days after completion of the modification.

Under EPA regulations, a modification was not deemed to occur if the source owner was able to offset an emission rate increase by reducing emissions elsewhere within the plant. This bubble concept allows a plant operator who altered an existing facility in a way that increased its emissions to avoid application of the standards by decreasing emissions from other facilities within the plant. This concept was rejected in the recent case of ASARCO, INC. v. EPA 11 ERC 1129 (D.C C.R., 1978) and EPA is currently in the process of removing this provision from the regulations.

It should be pointed out that the modification section of the NSPS regulations specifically exempt several types of activities including:

1. Routine maintenance, repair or replacement;
2. An increase in production rate accomplished without a capital expenditure;
3. An increase in the hours of operation;
4. Use of an alternative fuel or raw material if, prior to the date any standard under the part becomes applicable to that source type, as provided by §60.1, the existing facility was designed to accommodate that alternative use;
5. The addition or use of any system or device whose primary function is the reduction of air pollutants, except when an emission control system is removed or is replaced by a system which the Administrator determines to be less environmentally beneficial;
6. The relocation or change in ownership of an existing facility.

8.4 References *

1. Copy of applicable regulations sent from the Bay Area Air Pollution Control District in San Francisco, California.
2. Environment Reporter - State Air Laws, pp. 386:0501 et. seq.
3. Environment Reporter - State Air Laws, pp. 391:0501 et. seq.
4. Environment Reporter - State Air Laws, pp. 476:0501 - 476:0541
5. Copy of applicable regulations sent from the City of Cleveland
6. Environment Reporter - State Air Laws, pp. 491:0541 - 491:0741
7. Environment Reporter - State Air Laws, pp. 521:0521 - 521:0581
8. Environment Reporter - State Air Laws, pp. 546:0501 et. seq.
9. Environment Reporter - State Air Laws, pp. 451:0501 et. seq.

*NOTE - All literature references were verified through the applicable state and local air pollution control agencies.

9.0 HF MANUFACTURE EMISSION SOURCE SAMPLING AND ANALYSIS

There are three major groups of pollutants that can be encountered in HF manufacture.

1. Particulates, primarily CaF_2.
2. Fluorides, primarily HF and SiF_4.
3. Combustion related pollutants: SO_x, NO_x, and CO.

Table 9-1 presents a list of identified pollutants in HF manufacture and summarizes sampling and analysis techniques.

Determination of the emission rates is basically the same for all of the potentially emitted pollutants. It is necessary to measure the concentration of the pollutant by analyzing a sample which is representative of that in the duct or stack and which is characteristic of normal process operating conditions. It is also necessary to measure the volumetric flow rate of the gases in the duct or stack at the time of sampling. The substance mass emission rate is then calculated from the measured concentration and volumetric flow rate.

The following sections contain concise descriptions of the recommended sampling and analysis methods for the emissions from the HF manufacturing process. Not all methods have documented precision and accuracy and this information is provided only as available in the literature or determined by the contractor.

TABLE 9-1 SAMPLING AND ANALYSIS TECHNIQUES FOR THE EMISSIONS FOR HF

POLLUTANT	SAMPLING TECHNIQUE	ANALYSIS TECHNIQUE
Particulate, CaF_2, $CaSO_4$, fugitive SiO_2, $CaCO_3$ impurities.	Isokinetic with collection on glass fiber filters. Methods 5 or 17.	Gravimetric Method 5 or 17.
Total Fluorides, HF, SiF_4	Isokinetic with membrane filter and impingers with distilled water Method 13.	SPADNS - Zirconium Lake or specific ion electrode.
	Simplified Train	SPADNS - Zirconium Lake or specific ion electrode.
	Remote sensing	Infrared absorption and Emission Spectroscopy.
Sulfur dioxide SO_2	Sampled at constant rate through midget bubbler containing isopropanol and midget impingers containing hydrogen peroxide. Method 6.	Barium-thorin filtration
Carbon Monoxide CO	Integrated bag or continuous	NDIR (Non-dispersive infra-red)
Nitrogen oxides NO_x	Grab sample collected into evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution Method 7.	Colorimeteric using phenoldisulfonic acid (PDS) procedure.

9.1 Particulates

Particulate emission rates can be measured using the sampling and analysis techniques specified by Method 5 - Determination of Particulate Emissions from Stationary Sources[1] or Method 17 - Determination of Particulate Emissions from Stationary Sources (Instack Filtration Method).[2] Sampling and analysis procedures in both methods are essentially the same, the only difference being the location of the filter. Method 5 has a filter located outside the stack and thus the sample stream temperature must be maintained above the condensation point. Diagrams of the sampling trains for Methods 5 and 17 are presented in Figures 9-1 and 9-2, respectively.

9.2 Total Fluorides

The fluorides emission from HF manufacture expected to be in gaseous form consist of HF and SiF_4.

The emission rates of total fluorides can be measured using the sampling and analysis techniques specified in either Method 13 - Determination of Total Fluoride Emissions from Stationary Sources - SPADNS Zirconium Lake Method[3] or Method 13 B - Determination of Total Fluoride Emissions from Stationary Sources - Specific Ion Electrode Method.[3] The sample collection system and technique are similar to those of Method 5 for particulate.

Upon completion of sampling, the filter, impinger catch, probe wash and impinger wash are placed in a sample container. The weight of total fluorides collected is determined either by the SPADNS Zirconium Lake colorimetric method or by a specific ion electrode. To obtain the emission rate, the weight of the total fluorides is divided by the sample volume corrected to standard conditions and multiplied by the volumetric flow rate in the duct corrected to standard conditions.

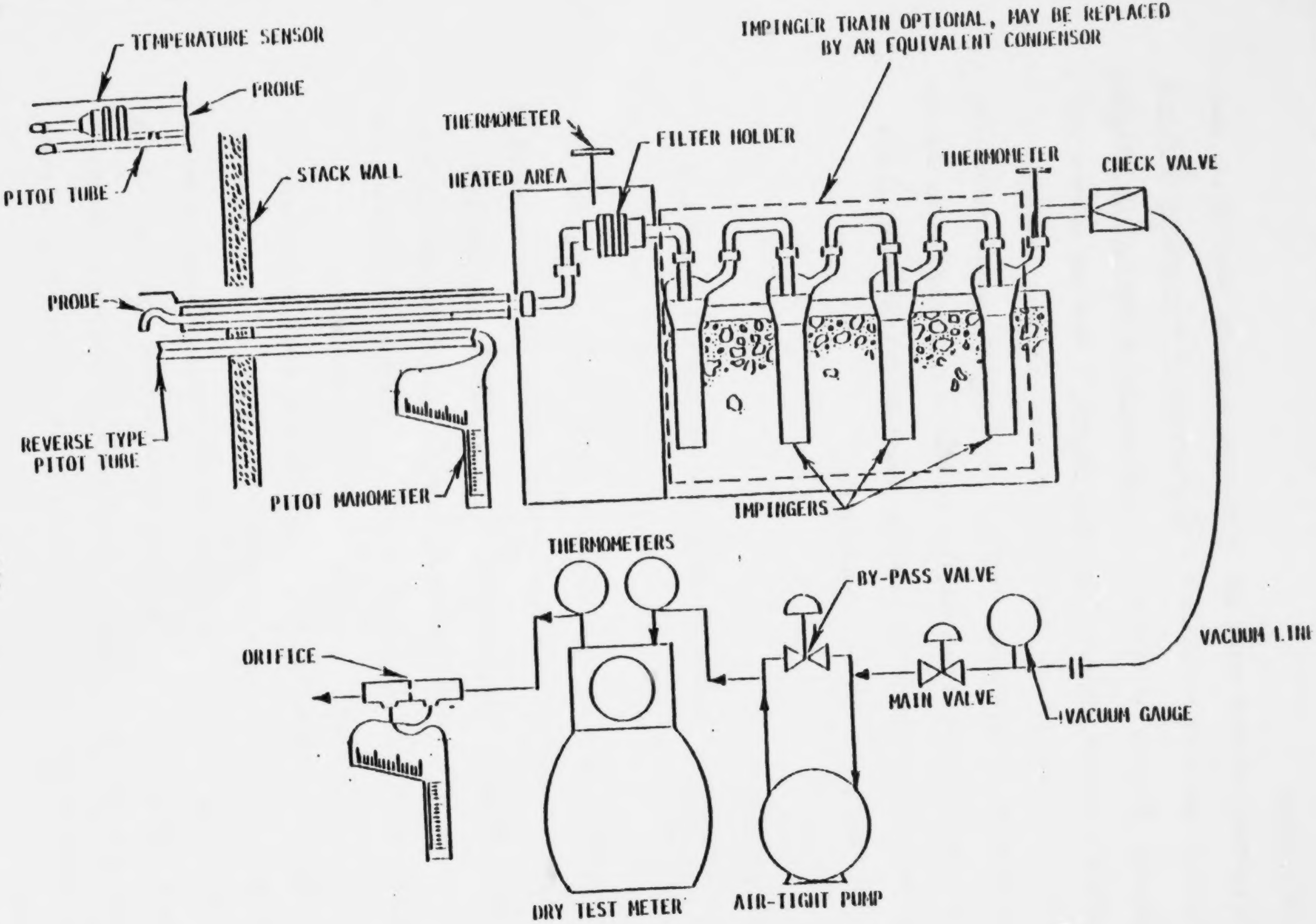

TEMPERATURE SENSOR
PROBE
PITOT TUBE
STACK WALL
PROBE
REVERSE TYPE PITOT TUBE
PITOT MANOMETER
THERMOMETER
HEATED AREA
FILTER HOLDER
IMPINGER TRAIN OPTIONAL, MAY BE REPLACED BY AN EQUIVALENT CONDENSOR
THERMOMETER
CHECK VALVE
IMPINGERS
THERMOMETERS
BY-PASS VALVE
VACUUM LINE
ORIFICE
MAIN VALVE
VACUUM GAUGE
DRY TEST METER
AIR-TIGHT PUMP

Figure 9-1: Method 5 particulate-sampling train

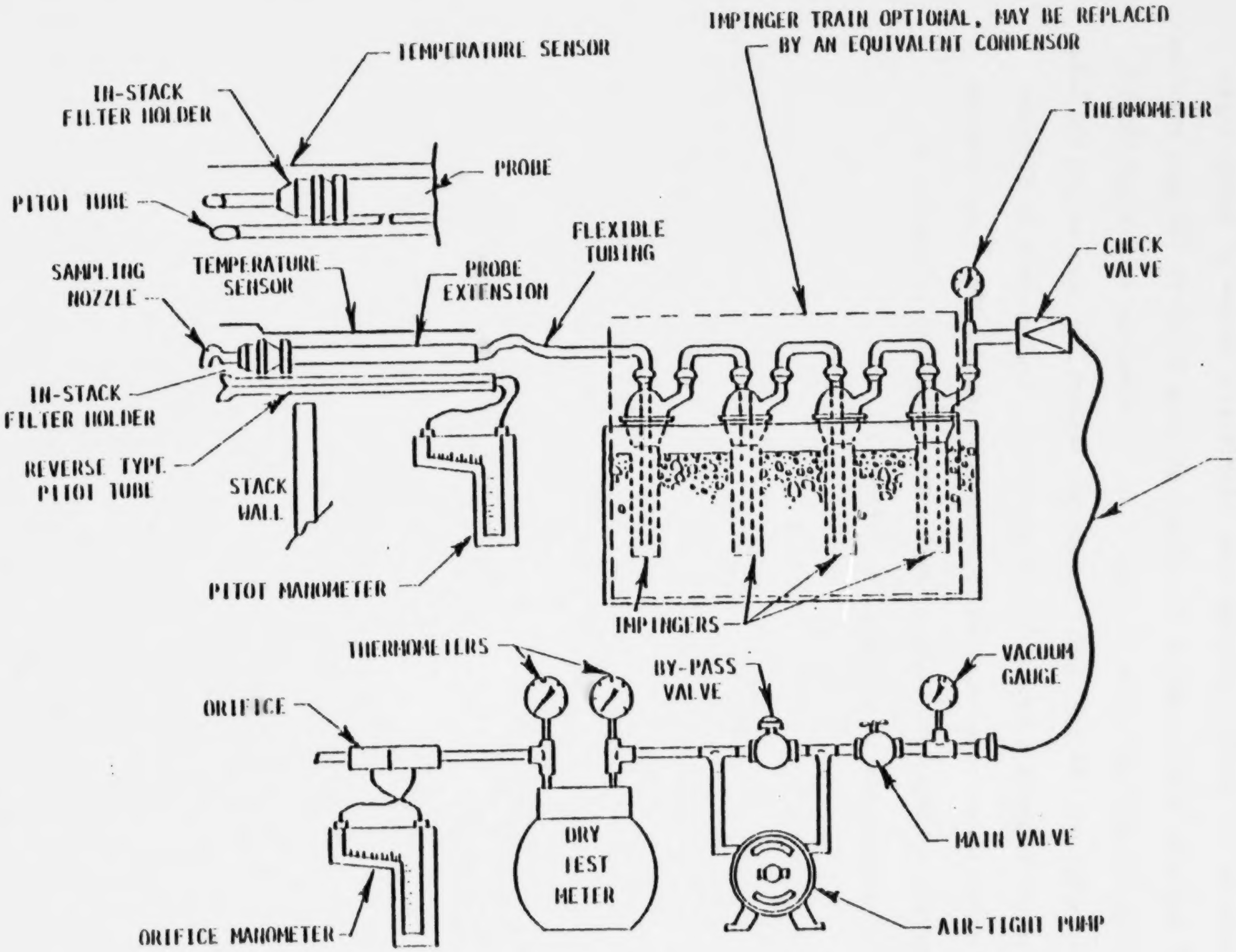

IMPINGER TRAIN OPTIONAL, MAY BE REPLACED BY AN EQUIVALENT CONDENSOR
TEMPERATURE SENSOR
IN-STACK FILTER HOLDER
PROBE
PITOT TUBE
THERMOMETER
FLEXIBLE TUBING
CHECK VALVE
SAMPLING NOZZLE
TEMPERATURE SENSOR
PROBE EXTENSION
IN-STACK FILTER HOLDER
REVERSE TYPE PITOT TUBE
STACK WALL
VACUUM LINE
PITOT MANOMETER
IMPINGERS
THERMOMETERS
BY-PASS VALVE
VACUUM GAUGE
ORIFICE
DRY TEST METER
MAIN VALVE
ORIFICE MANOMETER
AIR-TIGHT PUMP

Figure 9-2: Method 17 particulate-sampling train, equipped with in-stack filter

Analysis by the SPADNS Zirconium Lake colorimetric method of twenty replicate stack emission samples with a concentration range of 39 to 360 mg/l resulted in a relative standard deviation of 3 per cent. A phosphate rock standard with a certified value of 3.84 per cent fluoride was measured to have an average value of 3.88 percent fluoride based on 5 determinations. The accuracy of fluoride electrode measured has been reported to be in the range of 1 to 5 per cent in the concentration range of 0.04 to 80 mg/l. The collection efficiency of Method 13 sampling train is presented in reference 4.

9.2.1 TRC's Experience with Fluoride Sampling and Analysis

At the end of August 1977, TRC and EPA carried out the field program at CF Industries plant near Bartow, Florida. The purpose of the program was to validate the ROSE (Remote Optical Sensing of Emission) for the measurement of fluoride emission from the gypsum pond and to estimate the fluoride emission rate.

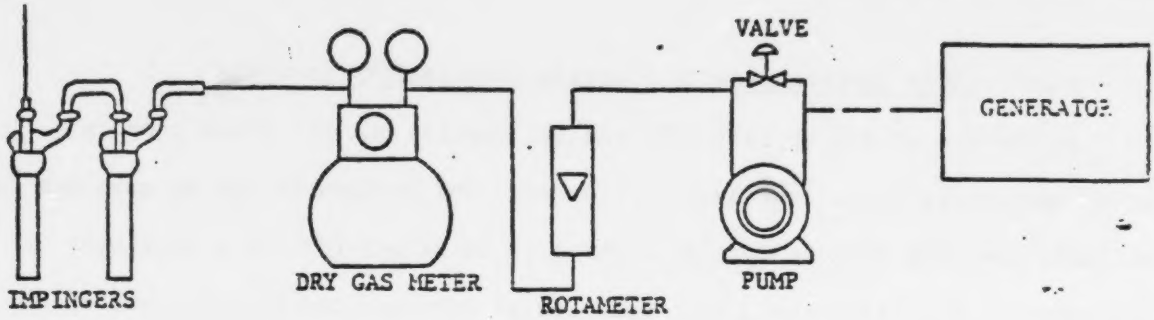
During the field program wet sampling/analysis was employed to determine fluoride emission at various points around the gypsum pound. The schematic of the sampling station is shown in Figure 9-3.

The results obtained during the field program were somewhat inconclusive and some questions were raised about the applicability of the simplified sampling train. Consequently, the calibration of the sampling train and fluoride analysis was carried out in controlled lab conditions to determine methods, precision and accuracy.

The ROSE method is based on absorpotion of hydrogen fluoride (HF) in 0.1N aqueous solution of sodium hydroxide and subsequent spectrophotometric determination of dissolved fluoride (using the SPADNS method). The experimental arrangement is shown in Figure 9-4.

The experimental arrangement incorporated a dynamic dilution system in which a stream of known concentration of HF was mixed with a stream of air taken from outside the building. Mixing occurred in a 7.5 ft. long section of a polyvinyl chloride duct 6 inches in diameter. Air velocity in the duct was 2,000 ft/min. The gases were absorbed with five impinger trains operated simultaneously. Each impinger train consisted of two impingers in series followed by a flow meter and a gas volume meter.

The influence of the following parameters on accuracy and precision were studied:


VALVE
GENERATOR
IMPINGERS
DRY GAS METER
ROTAMETER
PUMP

VERTICAL TRAVERSE SAMPLING STATION

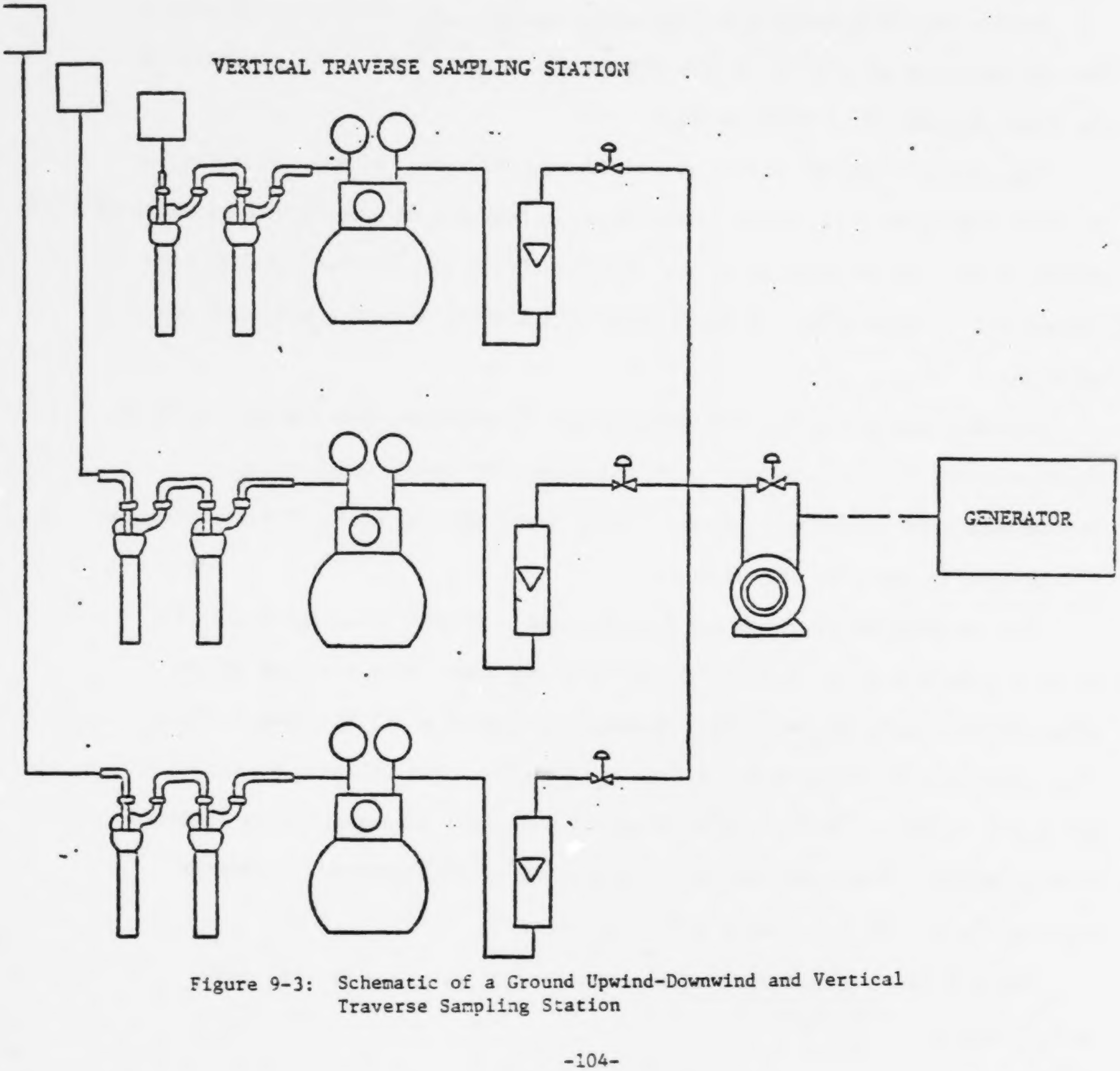


Figure 9-3: Schematic of a Ground Upwind-Downwind and Vertical Traverse Sampling Station

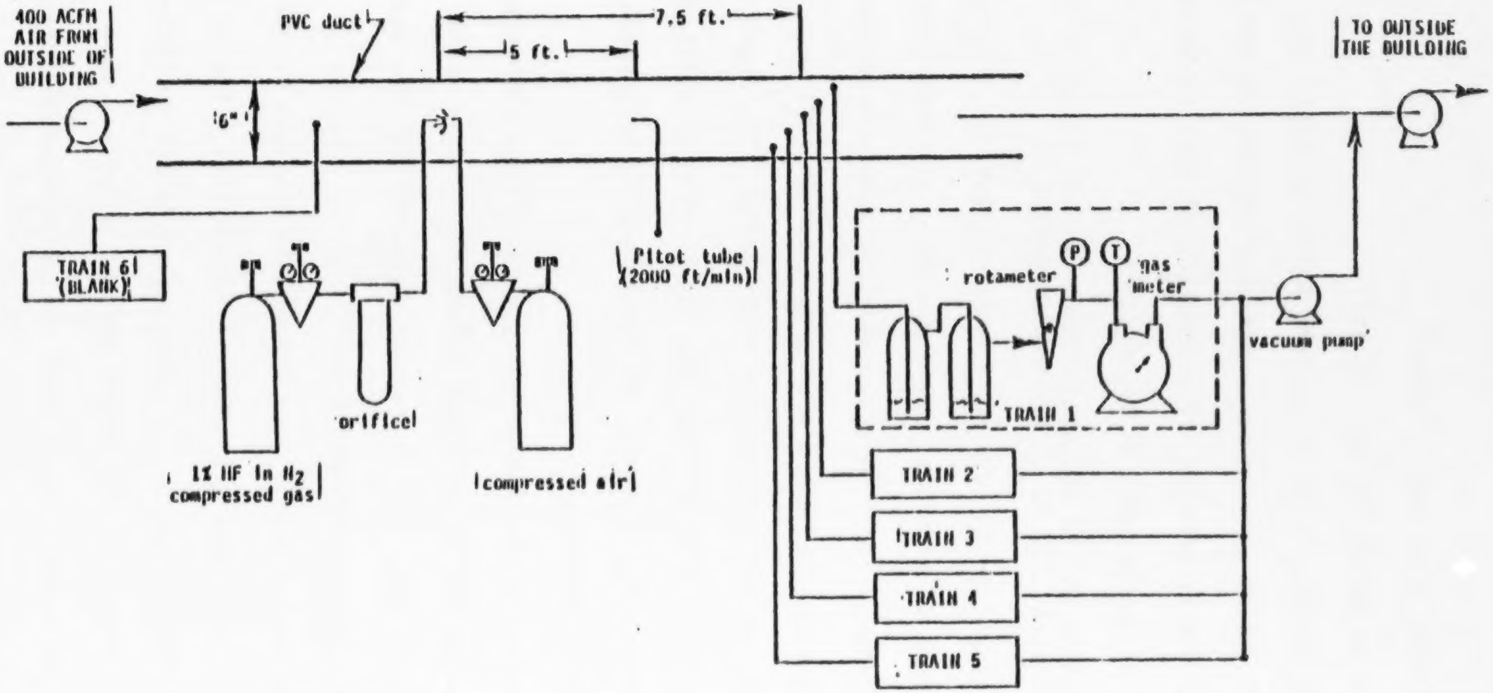

400 ACFM AIR FROM OUTSIDE OF BUILDING
PVC duct
7.5 ft.
5 ft.
TO OUTSIDE THE BUILDING
6"
TRAIN 6 (BLANK)
1% HF in H_2 compressed gas
orifice
compressed air
Pitot tube (2000 ft/min)
rotameter
P
T
gas meter
vacuum pump
TRAIN 1
TRAIN 2
TRAIN 3
TRAIN 4
TRAIN 5

Figure 9-4: Experimental Arrangement for Evaluation of Hydrogen Fluoride Sampling and Analysis

-sampling time (1 hr. to 2.5 hrs.)

-concentration of HF (50 ppb, 20 ppb)

-effect of impinger type (Greenberg Smith, standard tip)

-effect of tubing used in train assembly (Tygon, polypropylene)

-length of tubing used in train assembly (Tygon, polypropylene)

-presence of ice around the impingers

-liquid volume in the impingers (100, 80, 60, 40 ml in the first impinger, 100 ml in the second impinger)

-gas sampling rate through the train (21, 26, 36, 47 l/min)

The maximum number of identical tests was four, corresponding to four sampling trains operating simultaneously under the same conditions. The basic precision and accuracy of the method were determined in this way. Standard deviation was calculated for each group of four tests. The error for each group was expressed as a difference between the HF concentration as analyzed and the HF concentration as prepared. HF concentration as prepared was considered the true concentration.

Standard deviation of the results for groups of four simultaneous experiments ranged from 14% to 27%, with 18% as the average value. The error ranged from 1% to 35%, with an average value of 18%, and was positive for all the groups of experiments.

Different sampling conditions were often used for each of the four simultaneously operating sampling trains. This provided a faster way for evaluation of the effect of individual sampling variables on method accuracy and precision. A variable was considered to have no effect when the difference between the concentration of HF as analyzed and as prepared were within the experimental error.

Within experimental error, none of the variables investigated in this study was found to have an effect on the accuracy and precision of the method.

Over 90% (most frequently close to 100%) of the total HF absorbed in trains was absorbed in the first impinger whenever the initial liquid volume in the first impinger was above 40 mls. The only exception was noted when the sampling rate through the impingers was reduced to 21 l/min. Then 81% HF was absorbed in the first impinger. These preliminary results thus indicate that a reduction in sampling rate may reduce absorption efficiency probably due to less intense turbulence.

The conclusion of this study is that a simplified sampling train can be used for relatively simple and reasonably reliable determination of fluorides. It is recommended for field work when high accuracy is not required and the emission stream contains only gaseous fluorides.

9.2.2 Remote Sensing of Fluoride Emissions

During recent years, EPA's Environmental Sciences Research Laboratory at Research Triangle Park (ESRL/RTP) has been developing remote sensing techniques for gaseous pollutants. In the course of the measurement of fluoride emissions for a gypsum pond, described in Section 9.2.1, the ROSE System was used for identification of the fluoride species evolving from the pond. The major advantages of the ROSE System over wet sampling/analysis are[5]:

a. It gives a long path (up to 1 km) average concentration. This makes it a perfect tool for fugitive emission measurement.

b. It provides practically real time measurement requiring no sample handling.

c. It can distinguish between HF and SiF_4.

ROSE is a high-resolution IR spectrometer system. It utilizes a Fourier-transform interferometer to cover the 1.7-15 micron spectral region. This system has been installed in a van and can be used in the long-path absorption mode with a remote light source, or in a single-ended mode to observe emission signals from gases at elevated temperatures. All components necessary to obtain plotted spectra in the field are contained in a van.[6]

The main parts of the ROSE System are shown in Figure 9-5.

For absorption measurements over paths up to several kilometers, a Dall-Kirkham f/5 telescope with a 30 cm diameter primary mirror is used to collimate energy from a light source. Originally, a 1500°K blackbody was used as the source. Presently, a 1000 watt quartz-iodine lamp, which provides significantly more energy in the near IR and nearly as much energy in the middle IR as compared with the blackbody, is used. Generally, the light source and telescope system is installed in a small truck and driven to a desired location; a small generator powers the light source.

The remainder of the ROSE System has been installed in a 28-foot van. A telescope identical to that described above collects energy from the remote light

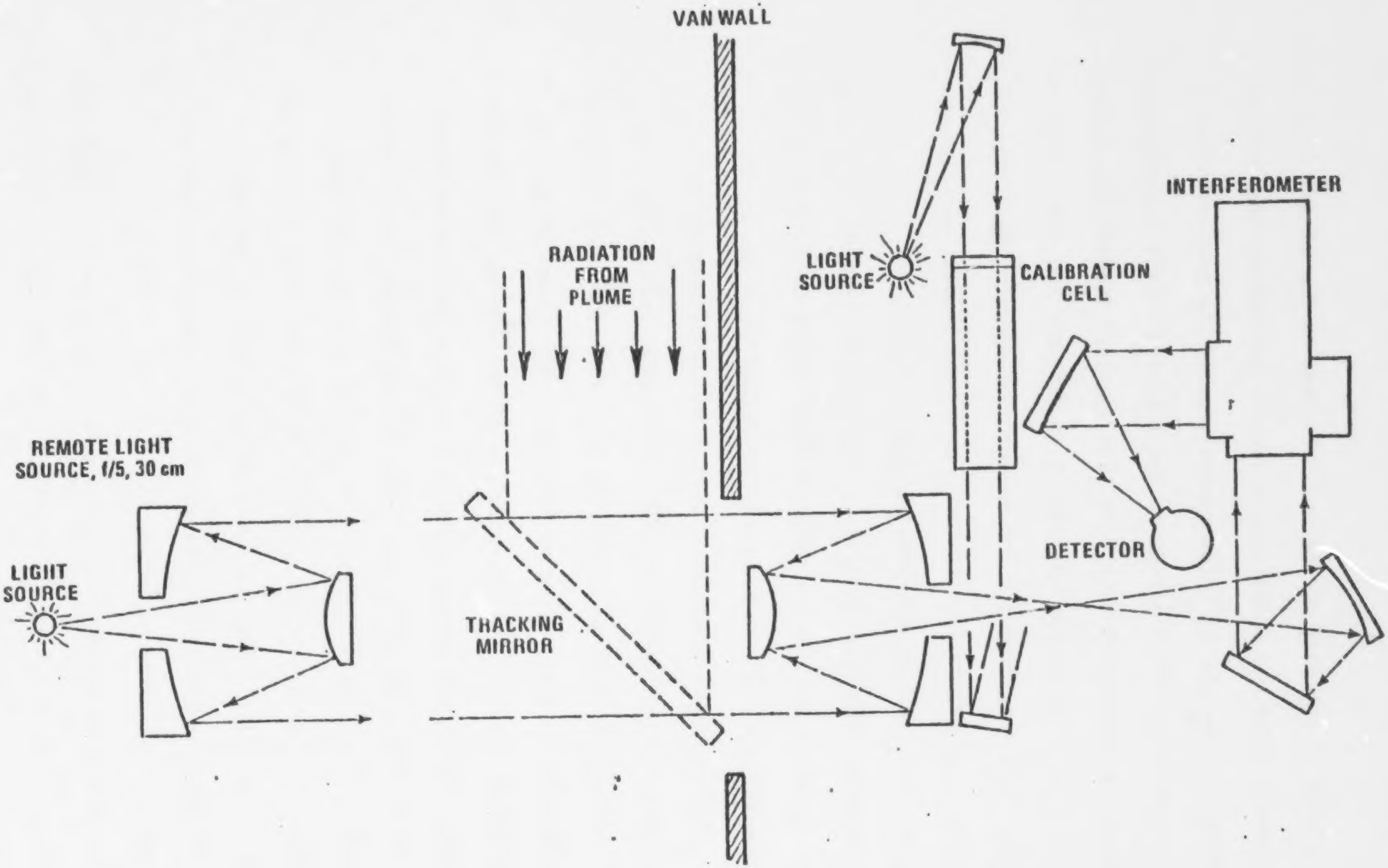

VAN WALL
RADIATION FROM PLUME
LIGHT SOURCE
CALIBRATION CELL
INTERFEROMETER
REMOTE LIGHT SOURCE, f/5, 30 cm
DETECTOR
LIGHT SOURCE
TRACKING MIRROR

Figure 9-5: EPA ROSE Infrared Spectrometer System

source through a port in the side of the van. To measure the signal from warm gases exiting a smoke stack, an elliptically shaped flat mirror (mounted on a platform attached to the van) reflects energy through the port into the telescope. The telescope focuses energy at the aperture of the interferometer. The interferometer and peripheral equipment is a standard Nicolet Instrument Corporation Model 7199 RT-IR System configured to fit into the van. Major components consist of a computer with 40K memory, dual-density disc with 4.8 million, 20-bit word capacity, teletype, paper tape reader, oscilloscope interactive display unit, and a high-speed digital plotter.

The interferometer itself is mounted on the telescope support structure. All other systems (except the plotter) are arranged in two 19-inch relay racks. Two beamsplitters, KBr and CaF_2, are currently available for use in the interferometer. A dual element, sandwich type detector is mounted in a liquid nitrogen dewar. For the 6000 to 1800 cm^{-1} region InSb is used and HgCdTe is used from 1800 to 600 cm^{-1}, with the two regions scanned separately.

Power for the ROSE system, including heating or air conditioning, is supplied by a 10 kw generator. During operation of the system, the generator is lowered from the van to the ground using an electrically-operated winch. This procedure is necessary to avoid electrical and mechanical interference with the operation of the interferometer. The entire system, including remote light source, can be placed in operation at a field site in about one hour under normal conditions. Auxiliary equipment carried in the van includes a weather station for recording wind velocity and temperature and a laser range-finder for measuring path lengths.

The first field use of the ROSE interferometer system was at a phosphate fertilizer plant gypsum pond. A series of these ponds are used at fertilizer plants for wastewater treatment. The ponds, which are generally rectangular in shape with boundary dimensions as long as a kilometer, are particularly suitable for long-path measurements. The particular environmental problem presented by these ponds is that they give off gaseous fluorides. In past studies using wet chemistry sampling methods, it had been possible to measure only total fluorides. Analysis of the pond chemistry indicates that expected gaseous fluorides would be SiF_4 and/or HF. Thus a study was undertaken at the C. F. Industries fertilizer plant near Bartow, Florida, to determine specifically which gaseous fluorides are emitted from the ponds.

A series of measurements were made at various locations around several ponds with path lengths ranging from 500 to 1000 meters. Typical spectra obtained are shown in Figure 9-6. The upper spectrum was taken over a 900 meter path at a location known to be free of HF. The middle spectrum was taken over an 860 meter path across a gypsum pond. Both spectra were taken with a resolution of 0.125 cm^{-1} (molecules $cm^{-2})^{-1}$ and a half-width of 0.04 cm^{-1}; the HF concentration was determined using the equivalent-width method. The calculations were carried out with an existing computer program. For the HF line shown, the path-averaged concentration was determined to be 45 ppb. (It was not possible to calibrate the HF spectrum with the sample cell method since our gas handling system is not resistant to HF.) Absorption due to the SiF_4 fundamental band centered at 1031.5 cm^{-1} could not be detected. Calibration spectra indicated that 0.5 ppb of SiF_4 would have produced about 4 percent absorption over an 860 meter path, and this value is taken as a reasonable lower sensitivity limit.

Contact with regulatory agencies and HF manufacture plants revealed no data on fluoride emissions from gypsum ponds. Although gypsum ponds used in HF manufacture probably generate less fluorides than phosphate fertilizer manufacture, measurement should be carried out to determine the environmental impact. Use of the ROSE System and simplified sampling train is recommended for the measurement program.

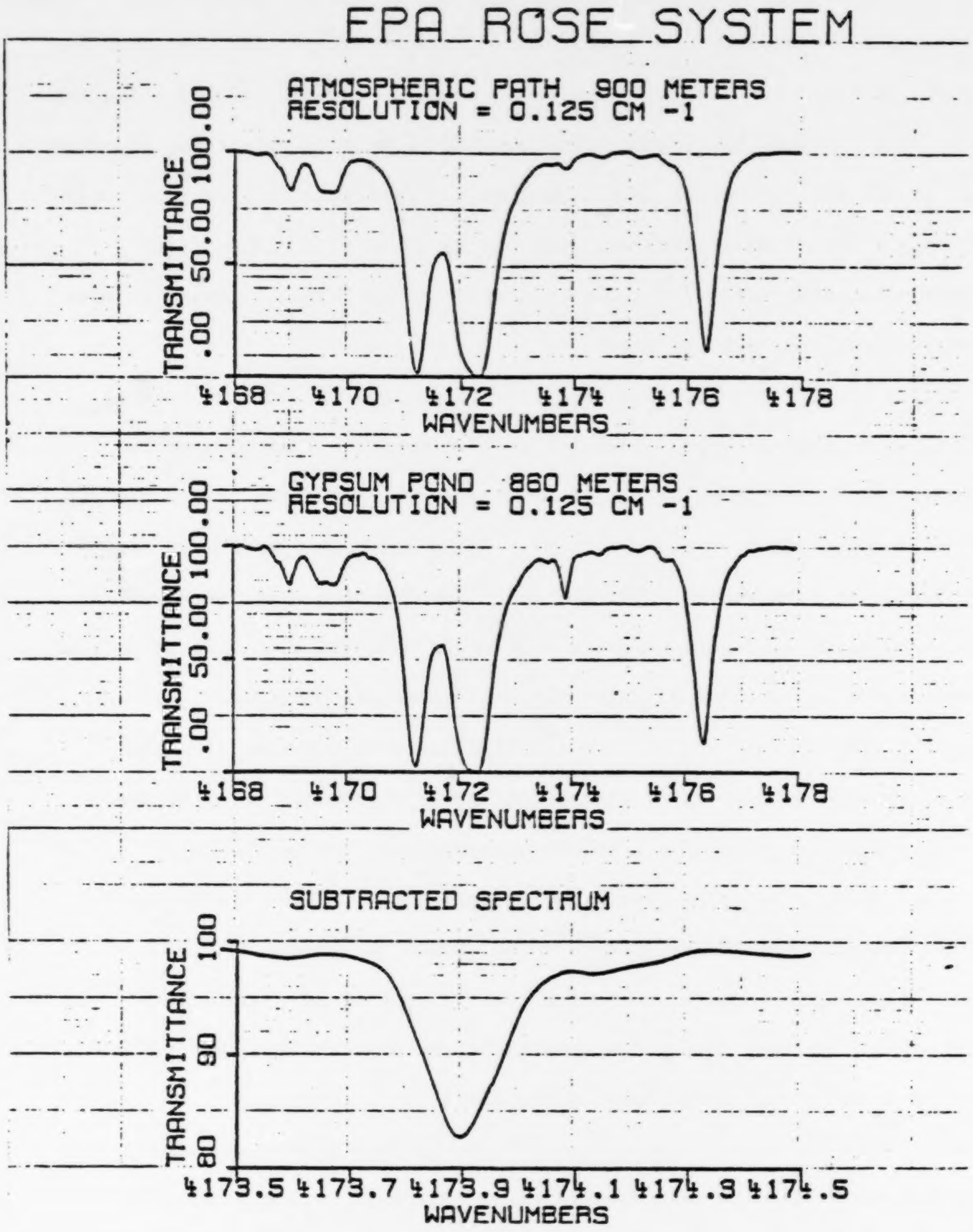


Figure 9-6: Gypsum Pond Spectra

10.0 ENVIRONMENTAL EFFECTS OF FLUORIDE EMISSIONS

Fluorine is considered a welfare-related rather than a health-related pollutant because it has no significant effect on human health in the concentrations found in the atmosphere even under the most adverse conditions. However, atmospheric concentrations which can exist around processes emitting fluorine compounds can adversely affect plants and animals, which may pose an indirect threat to our economy and general welfare.

In nature, fluorine is widely distributed in minerals such as fluorspar and fluoropatite, the prime constituent of phosphate rock. Atmospheric fluorine contaminants are emitted primarily from heavy chemical industries which utilize fluorine compounds as catalysts or fluxes. The major sources of these pollutants are phosphate fertilizer, aluminum and steel plants, and manufacturers of fluorinated plastics and fluorinated hydrocarbons. The effects of fluorides on vegetation have been known since the late 1800's, but it was not until the rapid industrial expansion of the 1940's that its effects were recognized as significant.[1]

10.1 Vegetation Effects

The severity of injury sustained by vegetation exposed to fluoride contaminants is dependent primarily on the form taken by the pollutant. Fluoride is taken up by absorption into the plant tissues, usually through the leaves, where it flows toward the margins and accumulates. This gradual accumulation, combined with the length of exposure and total fluoride concentration in the ambient atmosphere, determines the degree of injury. Gaseous compounds are probably responsible for most plant damage since they are easily absorbed. Most research to date has dealt mainly with exposure to gaseous fluorides such as hydrogen fluoride, fluorine, silicon tetrafluoride or fluorosilicic acid. Fluoride in particulate form is hazardous only when it is soluble and therefore able to be absorbed into the plant tissues.[1]

Susceptibility

Although all plants naturally contain varying amounts of fluorine, certain species are more susceptible to its effects than others. There are many factors involved in a plant's reaction to fluorides, often making it difficult to determine the exact cause of injury. Certain environmental factors such as rainfall, temperature and winds may result in injuries which are almost impossible to distinguish from pollution damage.[3] Table 10-1 is an example of the pollutant concentrations affecting both sensitive and resistant varieties of some economically important crops.

TABLE 10-1[2]

HYDROGEN FLUORIDE CONCENTRATIONS AND EXPOSURES FOR SENSITIVE AND RESISTANT PLANT SPECIES

Plant	Sensitive Varieties		Resistant Varieties	
	Concentration	Exposure	Concentration	Exposure
Corn	2 ppb	10 days	800 ppb	4 Hrs
Tomato	10 ppb	100 days	700 ppb	6 days
Alfalfa	100 ppb	120 days	700 ppb	10 days
Sorghum	.7 ppb	15 days	15 ppb	3 days

Most forage crops are fairly tolerant as are several species of vegetables and deciduous trees. Some species sensitive to fluoride are certain conifers, fruits, berries and grasses. These sensitive varieties generally exhibit damage at concentrations between 0.5 ppb and 1.2 ppb for several consecutive days.[4] In comparison, 5-10 ppm of fluoride are normally accumulated by plants in the absence of an atmospheric fluoride source.[1]

Injuries

Probably the most apparent effect of fluoride on vegetation is necrosis or tip-burn. This injury is characterized by discoloration around the edges of the leaves caused by the accumulation of fluoride in these areas. This is the most economically significant impact of fluoride contamination. Although necrosis does not necessarily harm the vegetation, the concentrations may be too high to be safely ingested by animals.[4] In addition, if the marketed portion of a plant is visibly damaged, it could result in great economic loss, even though actual injury to the plant may be slight.[1]

Exposure of vegetation of fluorides may also result in abnormalities or a decrease in reproductivity. Studies have shown abnormalities in growth including reduced leaf size, longer needles in Douglas Fir, and decreased tree growth. Most effects which limit or reduce growth are accompanied by visible injury; however, if the exposure to the fluoride source occurs late in the growing season, there may be little or no effect on the vegetation.[3]

10.2 Effect on Farm Animals

Atmospheric fluorides pose an indirect hazard to farm animals in their contamination of forage crops by absorption and accumulation in the vegetative tissues. Generally, the effects of fluoride contamination are felt only on farms situated near a fluoride-emitting facility or industries with inferior emission control systems. Since the inhalation of industrial emissions contributes very little to the total intake of atmospheric fluorides, soluble fluorides are more harmful to farm animals than the dust from phosphate rock or limestone.[4]

The fluorine ingested by animals is deposited almost entirely in the bones. While adult animals normally have concentrations of about 500 ppm in their bones, it takes concentrations of 5000 ppm before visible signs of the pollutant's effects are apparent.[3]

The studies performed on farm animals to date have revealed a sequence in which the effects of fluoride contamination appear. These are:

- Dental lesions, primarily in the incisors
- Hyperostosis, or bone overgrowth
- Lameness
- Loss of appetite
- Decrease in milk production
- Reduced reproduction

The last two effects are believed to occur from the decreased food intake caused by the loss of appetite. In one study performed, cattle were fed forage containing 600-1200 ppm of fluoride, resulting in a 50% decrease in food consumption due to their loss of appetite. Economically, this is the most serious effect of fluoride contamination in farm animals.[4]

A continuous intake of 40-50 ppm of fluoride eventually results in the destruction of incisors, meaning inhibited grazing and great economic loss. However, this damage occurs slowly; thus the economic impact would not reach its maximum until exposure had continued for about five years. Dental injury would also not be more likely to occur in young animals, and would not be expected in adults.[4] Table 10-2 lists the fluorine which can be ingested safely by livestock.

TABLE 10-2[4]

SAFE LEVEL OF FLUORINE IN LIVESTOCK FEED

Animal	Source Soluble Fluoride (ppm)	Rock Phosphate (ppm)
Dairy Cattle	30-50	60-100
Beef Cattle	40-50	65-100
Sheep	70-100	100-200
Swine	70-100	100-200
Chicken	150-300	300-400
Turkey	300-400	-

Fortunately, animals having high fluoride concentrations in their bones do not have contaminated meat or milk. Their loss of appetite will affect their production, but the pollutant is not passed on. Nursing calves do not suffer from fluorosis (abnormal calcification of the teeth) until they begin grazing contaminated forage.[2]

10.3 Effects in Man

Regardless of the source of the fluoride its effects are essentially the same; hyperostosis and fluorosis. Generally these conditions occur only in growing children.[3]

The current threshold limit value for hydrogen fluoride is 3 ppm, while the limit for particulate fluoride is 2.5 mg/m^3. Owing to these occupational limits, persons seldom are exposed to such concentrations, and very few cases of adverse effects from atmospheric fluoride occur, even in proximity to industrial sources. The maximum daily concentration inhaled near fertilizer facilities is about 150 µg which is insignificant when compared to concentrations of 1200 µg received from food and water.[2]

In man, the airborne fluorides are absorbed through the skin and from the respiratory tract and are accumulated in bones and teeth. The more soluble fluorine compounds are absorbed from the gastrointestinal tract into the blood much more readily than less soluble compounds. These are the forms that will accumulate in the bone structures.[2] Studies have revealed that the body is able to absorb 87% of calcium fluoride from cryolite, 62% of sodium fluoride, and 37% of calcium fluoride derived from bonemeal. About half of the absorbed fluoride is excreted, with the remainder being accumulated in the bones.[3]

Since research done to date indicates that airborne fluorides not not present a direct threat to man except from uncontrolled occupational exposures.

Their significant impact to man lies in the potential for economic loss by contamination of plants and animals.

10.4 Other Effects

Fluoride is capable of etching glass at concentrations of 590 ppb for a period of 9 hours and pronounced etching occurs at concentrations of 790 ppl for 14.5 hours. However, severe damage seldom or never occurs due to the emission regulations imposed on industry.[4]

Fluorides also have a damaging effect on the high silica brick lining of furnace walls used in aluminum processing.[4]

Hydrogen fluoride is especially significant in the reactions between fluorides and silicon compounds which result in damage to ceramics and glass.[3] However, it is very difficult to isolate the effects of fluorides from other background pollutants.

10.5 References

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2. Office of Air Quality Planning and Standards, 1976. Final Guideline Document: Control of Fluoride Emissions from Existing Phosphate Fertilizer Plants. Office of Air and Waste Management, U.S. Environmental Protection Agency, pp. 2-1 - 2-10.

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11.0 EMISSION REDUCTION WITH NEW SOURCE PERFORMANCE STANDARDS

11.1 Introduction

Model IV is a methodology developed by EPA's Emissions Standards and Engineering Division which quantitatively estimates the anticipated impact of new or revised standards of performance in reducing atmospheric emissions. Model IV mathematically relates emission producing activities, such as industrial growth, and offsetting emission control activities such as existing regulations, NSPS, and the Clean Air Act. The resulting net emissions are projected for target years.

Using Model IV, the differential in atmospheric emissions that could be expected with and without NSPS can be expressed and the potential for additional controls evaluated. For example, a maximum emission differential or NSPS impact would be observed for an industry for which a stringent standard of performance was technically feasible, but for which there were no existing state emission limitations. On the other hand, a minimum or zero emission differential NSPS or impact would be observed for an industry if a standard of performance representing best control technology was generally equal to existing state regulations. NPS would have few beneficial effects in the latter case in reducing emissions.

TRC in a 1976 EPA report[1] developed Model IV data and results for approximately 190 industrial catagories, including hydrofluoric acid.

Utilizing the best available 1978 data, TRC has updated the Model IV input variables to calculate the estimated impact of instituting New Source Performance Standards based on best available control technology.

11.2 Model IV - Background Information

The impact of new or revised standard of performance is expressed in Model IV as $(T_s - T_N)$

Where: T_s = emissions under baseline year control regulations.

T_N = emissions under new or revised standards of performance.

Factors such as increased production capacity, construction to replace obsolete capacity, control technology, and present allowable emissions are used to develop the above relationship. Table 11-1 defines these parameters used in the Model IV equations. From the input variables, T_s and T_N, the total emissions in the ith year under baseline year regulations and revised standards of performance, respectively, are calculated, where:

$$T_s = E_s K (A-B) + E_s K (B+C) \qquad (11\text{-}1)$$

$$T_N = E_N K (A-B) + E_N K (B+C) \qquad (11\text{-}2)$$

$$T_s - T_N = K (B+C) (E_s - E_N) \qquad (11\text{-}3)$$

Other related equations are:

1) Assumption of compound growth $B = A [(1+P\Delta)^i - 1]$ (11-4)

$C = A [(1+P_c)^i - 1]$ (11-5)

2) Assumption of simple growth $B = Ai \, P_B$ (11-6)

$C = Ai \, P_c$ (11-7)

Where i = elapsed time in years.

3) baseline year emissions $T_A = E_s KA$ (11-8)

4) Uncontrolled emissions $T_u = E_u K\ (A-B) + E_u K\ (B+C)$ (11-9)

5) For pollutants regulated under Sec. 111(d) of the Clean Air Act.

$$T_{NP} = E_{111(d)} K\ (A-B) + E_N K\ (B+C) \qquad (11\text{-}10)$$

Where $E_{11(d)}$ = allowable emissions as required by Section 111(d)

G_{ND} = total emissions in ith year under Section 111(d)

For these calculations the baseline year is defined as 1977 and the ith year, 1987.

TABLE 11-1

MODEL IV INPUT VARIABLES

T_s = total emission in i^{th} year under baseline year regulations (tons/yr)

T_N = total emission in i^{th} year under new or revised NSPS which have been promulgated in the j^{th} year (tons/yr)

T_U = total emissions in i^{th} year assuming no control (tons/yr)

T_A = total emissions in baseline year under baseline year regulations (tons/yr)

K = normal fractional utilization rate of existing capacity, assumed constant during time interval

A = baseline year production capacity (production units/yr)

B = production capacity from construction and modification to replacement obsolete facilities (production units/yr)

C = production capacity from construction and modification to increase output above baseline year capacity (production units/yr)

P_B = construction and modification rate to replace obsolete capacity (decimal fraction of baseline capacity/yr)

P_C = construction and modification rate to increase industry capacity (decimal fraction of baseline capacity/yr)

E_S = allowable emissions under existing regulations (mass/unit capacity)

E_N= allowable emissions under standards of performance (mass/unit capacity)

E_U= emissions with no control (mass/unit capacity)

For the purpose of this study, the i^{th} year is defined as 1987 and the j^{th} year, 1977.

11.3 Industrial Factors

K Factor

K is the normal fractional utilization rate of existing capacity. The fluorocarbon ban and aluminum inventory surplus have affected the production of hydrofluoric acid and this significant decrease is reflected in K Factor. In the baseline year, 1977, production of hydrofluoric acid was 74% of capacity, based on production and capacity data for the HF industry. In the following five year span, plants project a small or zero increase in production. In addition, major HF production facilities in Louisiana and Texas will be ceasing operations, and in 1982 utilization of 70% of the industry capacity is projected. The estimated K Factor for the entire 1977-1987 period is 73%.

P_C Factor

P_C, the construction rate to increase industry capacity, is expected to be zero during the ten year period 1977-1987. The 1977 baseline capacity of 369 thousands tons of hydrofluoric acid is not expected to be exceeded during the period.

P_B Factor

As with P_C; P_B, the construction and modification rate to replace obsolete capacity is projected to be zero during 1977-1987.

A Factor

The A Factor is the 1977 baseline year capacity. As previously stated, the 1977 capacity for the hydrofluoric acid industry is 369 thousands tons of anhydrous HF.

Assuming 99% particulate removal efficiency,

E_u = 3500 lb./ton 100% HF

For allowable emissions, the average process weight rate is calculated as:

$$\frac{\text{96 ton acid}}{\text{day}} \times \frac{\text{3500 lb. fluorspar}}{\text{ton acid}} \times \frac{\text{day}}{\text{24 hr.}} = \text{14,000/lb./ fluorspar hr.}$$

Allowable particulate emissions are determined for each state based on the above process weight rate and weighted according to the fractional capacity occurrence for 1977. Allowable emissions were calculated to be 19.5 lb./hr. It should be noted that West Virginia has no particulate regulations for the HF industry based on an inconsistency in the state air pollution law.

E_s is calculated for 19.5 lb./hr. and 96 tons of acid per day to be 4.9 lb./ton acid. However, 35 lb./ton HF is the best control technologically feasible. Therefore, $E_s = E_N$ as control regulations can only be set as low as current technology will permit.

Exit gas streams from the HF process are scrubbed with jets and sprays to remove SO_2 and fluoride emissions. The estimated removal efficiency for sulfur dioxide by the scrubber is 96% - 99%. Therefore,

$$E_N = 0.1 \text{ lb./ton } 100\% \text{ HF}$$

The allowable sulfur dixoide emissions from process systems vary from state to state. West Virgina, Louisiana, Ohio and New Jersey limit sulfur dioxide process emissions to 2000 ppm. Other states do not have any applicable regulations. Assuming an average kiln emission flow rate of 5000 scfm and an average capacity of 96 tons of acid/day for each of the eleven (11) existing HF plants, the allowable sulfur dioxide emissions can be calculated for the regulated states. For Louisiana, New Jersey, West Virginia, and Ohio, E_s equals 25 lb./ton 100% HF.

These limits for E_s are greater than E_u. Therefore, for all states the allowable SO_2 emissions are equal to uncontrolled SO_2 process emissions and $E_s = E_u$.

Particulate Emissions

Particulates are released during the drying of fluorspar. Literature values are not available specifically on particulate emissions for uncontrolled sources in hydrofluoric acid manufacture. However, use of a baghouse can achieve 99% particulate removal. In addition, particulate emissions for a well-controlled plant have been estimated at 20 lb./ton fluorspar.[2] Using 3500 lb. fluorspar/ton 100% HF, best available controlled emissions with a baghouse are:

$$E_N = 35 \text{ lb./ton } 100\% \text{ HF}$$

11.4 Emission Factors

Acid Production

Hydrofluoric acid is produced by the reaction of fluorspar with sulfuric acid in a rotary kiln. One ton of anhydrous HF requires 3500 lb. fluorspar (98% CaF_2) and 6400 lb. H_2SO_4. While the grade of HF acid produced varies, 95% anhydrous and 5% 70% grade acid is typical of plant production.

Fluoride Emissions

Uncontrolled fluoride emissions from a rotary kiln have been estimated at 50 lb./ton of acid.[2]

Therefore, E_u = 50 lb./ton acid.

The best available control technology for control of fluoride emissions is use of a wet scrubber j with a removal efficiency over 99%. E_N for the controlled emissions of fluorides is estimated at .2 lb./ton acid.

As there are no regulations for fluoride emissions (other than ambient air limitations), the allowable emissions of luorides, E_s, is equal to the uncontrolled emissions. Therefore,

$$E_s = E_u = 50 \text{ lb/ton acid.}$$

Sulfur Oxide Emissions

While the sulfuric acid in the hydrofluoric acid reaction produces a calcium sulfate slurry, sulfur in acid grade fluorspar creates sulfur dioxide emissions.

Fluorspar is approximately 0.03% sulfur content, assuming 3500 lb. fluorspar produces one ton of anhydrons HF, 1.05 lb. S or 2.1 lb. SO_2 are emitted per ton of 100% hydrofluoric acid. Therefore,

$$E_u = 2.1 \text{ lb./ton 100\% HF}$$

11.5 Results of Model IV Calculations

Table 11-2 summarizes the Model IV industrial and emission factors for the hydrofluoric acid industry.

TABLE 11-2

MODEL IV INDUSTRIAL AND EMISSION FACTORS - HYDROFLUORIC ACID

Pollutant	emission factors				growth rates		industry capacity		
	E_u	E_N	E_s	K	P_B	P_C	A	B	C
	lb/ton 100% HF				/yr	/yr	ton/yr 100% HF		
Fluorides	50	0.2	50	73%	0	0	369×10^3	0	0
Sulfur oxides	2.1	0.1	2.1	73%	0	0	369×10^3	0	0
Particulates	3500	35	35	73%	0	0	369×10^3	0	0

Utilizing the input parameters outlined in Table 11-2, the 1987 impact of new source performance standards, $T_s - T_N$, was calculated to be zero for the hydrofluoric acid industry. This is due to the projected lack of increase in production capacity, a result of the fluorocarbon ban and aluminum inventory surplus.

In addition, a review of emissions control on an industry-wide basis indicates that most plants are currently utilizing best control technology (e.g. - baghouse and scrubbers). There is not enough data on HF and fugitive emissions to draw a clear conclusion on plant emissions, but it appears that little pollution reduction would be achieved by retrofitting existing plants.

11.6 References

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2. Compilation of Air Pollutant Emission Factors (2nd Ed.) EPA Publication No. AP-42, April 1973.

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